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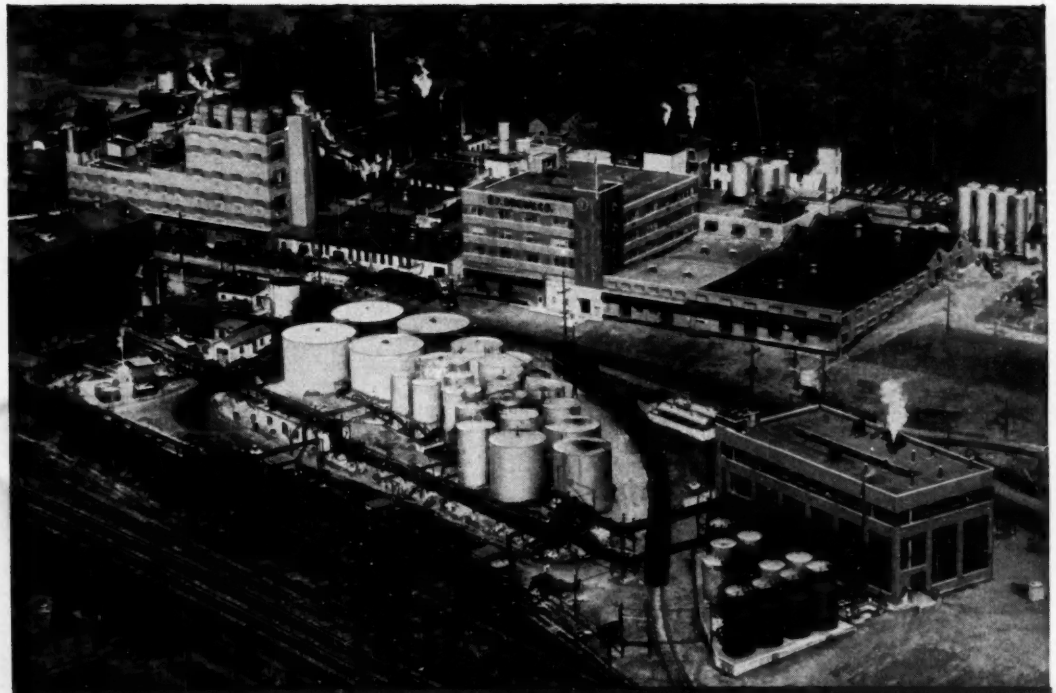

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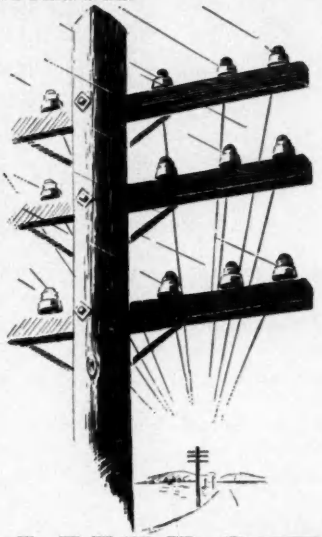

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TEXTILE RESEARCH JOURNAL

VOL. XXI, No. 4 April, 1951

The Strength and Weakness of Cotton Fibers*

Helmut Wakeham and Nancy Spicer

Textile Research Institute,† Princeton, New Jersey

Abstract

The structural reversals in cotton fibers are a preferred location of break when the fiber is ruptured in tension. With the aid of a polarizing microscope, observations were made of the fraction of fibers breaking at the reversals under various conditions of moisture content, specimen length, and chemical treatment. It is concluded that the cellulose in the region of the reversals is more highly crystalline than the cellulose between the reversals. The cause for breakage at the reversals is then explained on the basis of internal stresses at these points which cause the fiber to tear apart when tension is applied. The weak places between reversals which give rise to fiber rupture are believed to be at structural defects or thin places. The mean breaking stresses for fibers breaking *at* the reversals vary significantly from those for fibers breaking *between* reversals for some varieties of cotton. The distributions of weak-spot location and strength for reversals and structural defects are discussed for three varieties.

Introduction

A fundamental knowledge of the weak places in textile fibers as well as information on the mechanism of fiber rupture are basic requirements in fiber science and technology. Such information is essential to an intelligent program for the development of improved fibers by the cotton breeders, various natural-fiber producers, and synthetic-fiber manufacturers. It is also necessary in any fundamental study of the factors contributing to yarn and fabric properties. For these reasons the Textile Research Institute has engaged in an investigation of the elements of strength and weakness in textile fibers. Cotton has been selected as an initial example for study because of the many elements of weakness which each single fiber contains. The present paper on the nature of weakest links in cotton fibers reports some of the preliminary work in a more general investigation of the mechanism of fiber rupture.

Cotton with increasing specimen length exhibits a relative loss in fiber strength which is greater than

* Presented at the 21st Annual Meeting of Textile Research Institute, New York City, Nov. 16, 1950.

† This work, initially sponsored by The Textile Foundation, is now supported by the general research fund of Textile Research Institute.

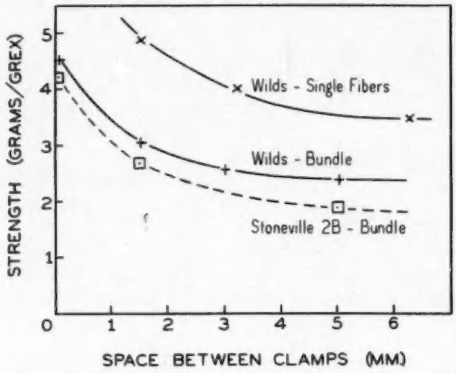

FIG. 1. *Effect of specimen length on cotton-fiber strength.*

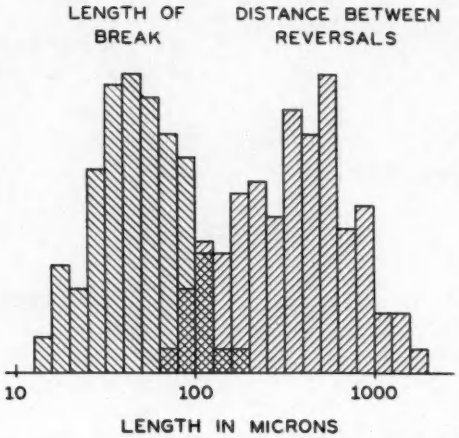

FIG. 2. *Distributions of the length of fiber involved in the break and of the distance between reversals for Wilds cotton.*

that of any other textile fiber. Wool and other natural fibers show appreciably lower tensile strengths at 10-mm. than at 1-mm. specimen lengths, in some cases as much as 10% lower. Synthetic fibers show a much smaller drop in strength. But the observed strength of cotton at a specimen length of 10 mm. may be more than 50% lower than the strength at 1-mm. test length (Figure 1). Although evaluations of this type are frequently made with fiber bundles, single-fiber test results support the observations with bundles and indicate that the loss in strength is inherently a fiber property. This great decrease in strength with long cotton specimens is undoubtedly due to a very high frequency of weak linkages along the length of the fiber.

It is widely believed that the weakest links in cotton fibers occur at the structural reversals first studied extensively by Balls and Hancock [3] in 1926. In the cotton fiber the cellulose molecules and bundles of molecules, or fibrils, instead of lying parallel to the long axis of the fiber, spiral around this axis in a helical manner. A fiber reversal occurs at those points where the direction of rotation of the cellulose about the fiber axis changes from a Z-direction to an S-direction, or *vice versa*. The reversal can be readily located in the natural, unswollen fiber by observing it with a microscope using elliptically polarized light.* (See Figure 3A.) Under these conditions the interference colors for the Z and S rotations are complementary, and the point at which the color changes indicates the reversal [9].

Cotton-fiber reversals are randomly spaced along the length of the fiber—approximately 100 to the inch—although the average distance between reversals appears to vary somewhat with variety. A distribution of distances between reversals is of the log-normal type shown in Figure 2. This statement implies only that there is a minimum distance between reversals, probably determined by the length of the reversal itself, and that the probability of finding an adjoining reversal at a distance greater than the minimum exponentially approaches unity.

Experimental Procedure

In order to determine the part cotton-fiber reversals play in fiber rupture, it must be possible to distinguish between breaks which do or do not involve a reversal. As implied above, this differentiation can be accomplished by merely examining corresponding broken ends of the fiber under a microscope used with a quarter wave red plate so as to produce elliptically polarized light. If the two broken ends of the properly oriented fiber in the field appear the same color, the break took place *between* reversals. If the two ends appear differently colored—*e.g.*, orange and blue—the break occurred *at* a reversal. Examples of these two types

* For a description of elliptically polarized light, the reader is referred to any standard textbook on physical optics, such as "Introduction to Physical Optics," by J. K. Robertson, 3rd Ed., New York, D. Van Nostrand Co., Inc., 1942.

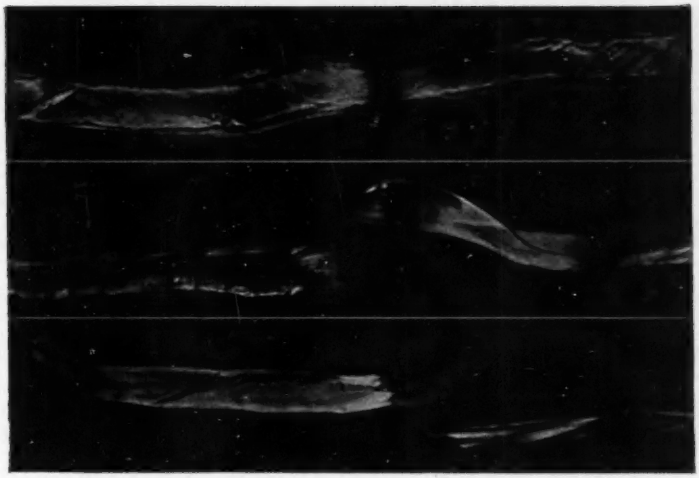

Fig. 3. *Photomicrographs of cotton fibers using elliptically polarized light. (Magnification approximately 600 ×.)* A *(top)—Fiber reversal, showing change of spiral orientation.* B *(middle)—Fiber broken at the reversal.* C *(bottom)—Fiber broken between reversals.*

of breaks are shown in Figure 3 (B and C). From these photographs it is quite apparent that not all fibers break *at* a reversal.

The existence of cotton-fiber breaks *between* structural reversals does not eliminate the possibility that fibers may break preferentially *at* the reversals. Such a preference can be established by examining many fiber breaks, but only if some previous knowledge of the expectancy of either type of break is available. In the discussion below, all breaks involving a reversal in *any* way have been classified as breaks *at* the reversal. Even if the reversals were not weak places in the cotton fiber, some of them would be involved in the fiber break simply by chance because there are so many of them along the length of the fiber. On this basis the fraction of fibers breaking *at* a reversal would be the ratio of the length of fiber involved in a broken place to the mean distance between reversals. From microscopic measurements this ratio turns out to be less than 0.15 (see Figure 2) so that an observation of more than 15% of the fiber breaks involving a reversal may be taken as evidence of an unusual weakness in the fiber *at* the reversal. Furthermore, from a statistical significance test, it can be shown that if half of the breaks involve reversals, it is only necessary to examine 50 fibers in order to conclude, with a 95% probability of being right, that the fiber breaks preferentially *at* the reversal.

It is possible from the information outlined above to establish a method for the investigation of the fiber reversal as a weak link. From determinations of the fractions of fiber breaks taking place at this position for various fibers under various conditions, certain information concerning fiber reversals and the contribution they make to fiber strength has been obtained. These observations are summarized in the Results section.

Each fraction (percentage) of fibers breaking *at* the reversal reported is based on the observation of at least 100 fibers and in some cases as many as 400. The fibers were selected from a standard length array prepared with a Suter-Webb cotton-fiber sorting apparatus [1], the length chosen being that corresponding approximately to the staple length or upper-quartile mean. It was noticed that the sorting operation yielded a well-blended fiber sample: the random selection of 100 fibers from such a sort gave a fraction of mature fibers which agreed very well with a standard maturity count obtained by the preferred A.S.T.M. method in which the fibers are swollen in 18% sodium hydroxide solution [1].

The selected fibers were broken in one of two ways —by hand or by a single-fiber stress-strain test. In

TABLE I. EFFECT OF VARIETY ON LOCATION OF BREAK AND MEAN BREAKING STRENGTHS (T.R.I.-SCHAEVITZ TESTER, 70°F, 65% R.H., EXCEPT WHERE NOTED)

Variety	Staple length (in.)	Specimen length (in.)	Breaks *at* reversal (%)	Strengths * for breaks: *At* reversal (g./grex)	Strengths * for breaks: *Between* reversal (g./grex)	Difference in strength (%)
Stoneville 2B	1 1/8	1	46	1.28	1.30	+ 2
Wilds	1 1/8	1	47	1.74	1.50	−13
Wilds	1 1/8	1/4	33	3.16	2.76	−13
Sak	1 1/16	1	47	2.64	2.84	+ 8
Hopi Acala 50	1 3/32	1	39	1.64	1.82	+11
Empire	1	3/4	49	1.37	1.70	+25
Empire (35% R.H.)	1	3/4	31	1.19	1.26	+ 6
Lockett 140	7/8	5/8	35	2.13	2.28	+ 7
Unknown *A* (28% mature)	7/8	5/8	41	1.73	1.82	+ 5
Unknown *B* (79% mature)	1 1/8	1	40	1.54	1.52	− 1

* Mean fiber strengths. The coefficient of variation for these breaking-stress values is about 40% of the mean.

both methods the fibers were first mounted at each end with Duco cement on small film tabs approximately 1/4 in. by 1/2 in. in size. In the hand method the fiber was slowly pulled apart by sliding the tabs apart on a microscope slide. In the machine method the fiber was mounted in the T.R.I.-Schaevitz tester previously described [12] and broken at a constant rate of extension of 20% per min. No effect of the method of break on the fraction of fibers breaking *at* or *between* the reversals was observed.

In those experiments in which the fibers were broken on the T.R.I.-Schaevitz tester, the breaking loads and breaking-stress values of the fibers were also determined. The breaking-stress values were obtained by dividing the breaking loads by the mean grex values of the individual fibers determined from a vibroscope measurement which has been described elsewhere [4, 5]. The purpose of quoting stress values instead of breaking loads is to permit comparison of mean values for fiber groups of different types and varieties.

Results

The results of observations made in the manner described above and shown in Tables I–IV permit the following statements concerning the location of break in cotton fibers to be made:

1. Of several fiber varieties investigated at reasonably long lengths and 65% R.H., about half of the fibers broke *at* structural reversals (Table I). This fraction is sufficiently greater than the theoretical value of 15% to permit the definite statement that reversals constitute a weak link in the chain.

2. There is no significant relationship between fibers of different cross-sectional shapes or maturities and the fraction of fiber breaks *at* reversals. The cross-sectional shapes of fibers were obtained by observing the color of the fiber in longitudinal view when properly oriented in a polarizing microscope with elliptically polarized light. Classification was made into linear, elliptical, and roundish fibers, as defined in the A.S.T.M. specifications [1]. In this grouping the linear fibers would ordinarily be called immature and the elliptical and roundish fibers mature. Of the more than 1,000 fibers examined in all the varietal groups listed in Table I, 43% of the linear, 46% of the elliptical, and 42% of the roundish fibers broke *at* reversals. Although there are approximately three times as many elliptical fibers as roundish ones in a common cotton sample, there is no significant difference in the location of break for mature and immature cotton fibers.

3. Increasing the specimen length increases the fraction of breaks involving reversals (Table II). This observation gives additional evidence that the fiber reversals are the possible locations of weak places in the fiber because increasing the specimen length directly increases the number of reversals available to act as the weakest link. This result also bears certain implications concerning the distribution of weak places occurring *between* the reversals, which will be discussed later.

4. Increasing the moisture content of the cotton increases the fraction of breaks involving reversals (Table III).

5. Treatments which modify the cellulose structure or damage the fiber so as to reduce its strength de-

TABLE II. Effect of Specimen Length on Location of Break (70°F, 65% R.H.)

Specimen length (in.)	Breaks *at* reversal (%) for: Stoneville 2B	Wilds	Sak	Hopi Acala
1/16	—	—	32	19
1/8	—	33	36	20
1/4	35	34	38	—
1	47	47	46	39
1 1/4	—	—	53	—

TABLE III. Effect of Moisture on Location of Break

Cotton sample	Moisture condition	Breaks *at* reversal (%)
Sak	Dry	35
Sak	35% R.H.	34
Sak	65% R.H.	46
Sak	In water	49
Empire	35% R.H.	31
Empire	65% R.H.	49

TABLE IV. Effect of Fiber Treatment on Location of Break

Fiber and treatment	Breaks *at* reversal (%)
Sak, 1/4-in. specimen length	
Conditioned at 70°F, 65% R.H.	36
Water-wet	49
Swollen in 18% NaOH	18
Swollen, dried, conditioned	18
Unknown variety, 1/4-in. specimen length	
Control	40
Hydrolyzed in 1*N* HCl, 60°C	26
0.35% formaldehyde	24
6.5% melamine resin	40

crease the fraction of fiber breaks involving reversals (Table IV). Swelling the fiber in strong caustic greatly reduces the tendency to break at reversals. Treatment with formaldehyde in the vapor phase to introduce as little as 0.35% fixed formaldehyde decreases not only the strength of the fiber but also the fraction breaking at the fiber reversals. Mildly hydrolyzing the fiber for 18 hrs. in 1*N* hydrochloric acid solution at 60°C reduces the fraction of fibers breaking *at* the reversal from 40% to 26%. On the other hand, treatment with 6.5% melamine resin in such a way as to produce no appreciable loss in fiber strength does not affect the location of breakage.

6. The mean breaking strength of cotton fibers breaking *at* reversals does not differ greatly from those breaking *between* reversals (Table I). Apparently there is a varietal difference in this respect. In some varieties the fibers breaking *between* reversals have an average strength higher than the average for those breaking *at* the reversals. With Wilds cotton the converse seems to be the case, whereas Stoneville shows no difference. Attention is also called to the observation for Empire cotton that increasing the moisture content also increases the mean breaking stress for fibers breaking *between* reversals much more than that for fibers breaking *at* the reversals.

Discussion

One of the most interesting of the observations summarized above is that increasing the moisture content of the cotton fiber increases the fraction of fibers breaking *at* the reversal (Table III). Now it is well known that increasing the moisture content of cotton in the range between 35% and 65% R.H. also increases the strength of the cotton fiber [7]. In some way or another this effect takes place by strengthening the weakest linkages, which have been shown to involve fiber reversals, at least in some cases. But if the reversals are preferentially affected in this manner, the fraction of breaks *at* the reversals would be expected to *decrease* rather than to *increase*. The facts thus indicate that the moisture affects primarily those weakest linkages which occur *between* the reversals. Furthermore, x-ray and structural considerations suggest that the moisture effects take place mainly in the less ordered or noncrystalline regions because water molecules cannot readily enter the crystalline cellulose [6]. Hence, it is logical to conclude that the reversals, which are not preferentially strengthened, are more highly crystalline than is the remainder of the fiber.

The above considerations suggest that the increase in moisture should preferentially increase the breaking stress for those fibers breaking *between* reversals. Such an effect is observed for Empire fibers broken at 35% and 65% R.H. (Table I). The increase in breaking stress with increasing moisture content for those fibers breaking *between* reversals is 2.5 times that for the fibers breaking *at* reversals.

The conclusion of higher crystallinity at the reversals is further supported by the experiment in which fibers were mildly hydrolyzed. The acid-

catalyzed hydrolysis reaction presumably takes place first in the less ordered regions, cutting the cellulose chains in two in these areas. If the reversals are more crystalline than the rest of the fiber, then the fibers, being preferentially damaged by the acid hydrolysis *between* the reversals, should show a lower number of breaks *at* the reversals. Such was found to be the case. A cotton sample showing 40% fibers breaking *at* the reversals before treatment showed only 26% fibers breaking *at* the reversals after an 18-hr. hydrolysis in 1*N* hydrochloric acid at 60°C (Table IV).

This conclusion also raises the question concerning the reason why fibers tend to break *at* reversals. If the reversals are more crystalline than the rest of the fiber is, they might be expected to be exceptionally strong rather than weak. The evidence in Table I, as well as the fact that fibers do preferentially break *at* the reversals, precludes the possibility that reversals are exceptionally strong.

The experiment with caustic-swollen fibers (Table IV) suggests that fibers break *at* reversals because the structure at these points is already strained, so that additional load causes the fibers to tear apart at one of these points. It is known that swelling in strong caustic and subsequent removal of the caustic by washing out changes the structure of the crystalline portions of native cellulose. It may therefore be assumed that the 18% sodium hydroxide treatment reduces the number of breaks *at* the reversals by affecting the structure of the reversals themselves. If the cellulose structure in the region of the reversals is under an internal stress, swelling the cellulose would permit the relaxation and removal of these internal stresses and would eliminate the cause of preferential breakage at the reversals. The observed fraction of breaks *at* the reversal (18%) for the caustic-swollen fiber is not significantly different from the theoretical value of 15% based on a chance involvement of the reversal. The hypothesis that cotton fibers break *at* reversals because these points are already internally stressed is thus supported by the experimental evidence.

Although it has not yet been possible to perform the experiment, one way to check this hypothesis would be to examine cotton fibers from the unopened boll which had been broken before drying the first time. Presumably, these stresses *at* the fiber reversal are set up during the initial drying of the cotton-fiber cell.

Both Balls [2] and Meredith [8] have suggested that the cotton fiber may be internally stressed *at* the reversals. Meredith proposed further that this possibility may explain the observation that fibers with higher helical angles are weaker fibers. In other words, the tearing tendency *at* the reversals will be less in those cases in which the angular change in direction *at* the reversals is also less.

But what about the breaks which occur *between* reversals? What is the nature of these weak links?

As a result of the observations on reversals, it seems reasonable that the breaks occurring *between* reversals are those caused by real structural defects and thin places in the cotton fiber. Just as there are distributions [10] of locations and strengths for the weakest links *at* reversals, so there are also distributions of locations and strengths for the weakest links *between* reversals. The increase of breaks *at* reversals with increasing specimen length (Table II) indicates that on the average the structural weak links are somewhat farther apart than the reversals are. On the other hand, it must be remembered that the distributions of these two types of weakest linkages are imposed upon the same fiber length. There is thus a fair probability that the location of a structural defect may coincide with that of a reversal. This possibility greatly complicates the problem of finding out more about the weak places by the experimental methods now being used.

Furthermore, the results of Table I indicate that there may be varietal differences in the relative distributions of strengths for the two types of weakest linkages in the fiber. In some varieties the fibers breaking *at* reversals are on the average weaker than those breaking *between;* in others the converse is true.

TABLE V. COMPARISON OF WILDS, SAK, AND HOPI ACALA 50 COTTONS

Property	Wilds	Sak	Hopi Acala 50
Pressley strength		(g./grex)	
Conventional test	4.4	5.1	5.3
5-mm. space	2.3	3.1	2.3
1-In. fiber strength		(g./grex)	
Breaks *at* reversal	1.74	2.64	1.64
Breaks *between* reversal	1.50	2.84	1.82
Reversals per mm.	2.5	2.3	1.7
Breaks *at* reversal (¼ in.)	33%	36%	20%
Breaks *at* reversal (1 in.)	47	46	39

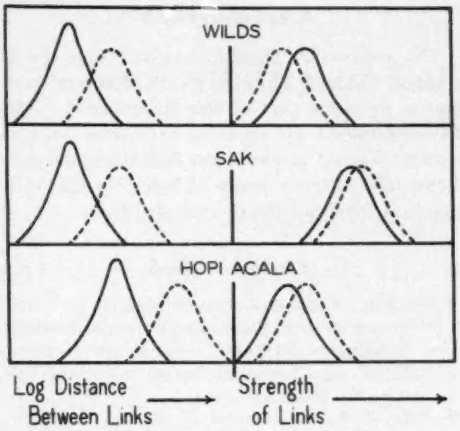

Fig. 4. *Probable arrangement of position and strength distributions of weak links in cotton fibers. Solid lines are for structural reversals; dotted lines are for structural defects between the reversals.*

Thus it is that the strength of a cotton fiber is determined by the weakest link available from a combination of no less than four probability factors involving the locations and strengths of at least two types of weakest linkages. Is it any wonder, then, that the observed breaking strength of cotton fibers varies as greatly as it does from one fiber to the next?

It is interesting to speculate somewhat concerning the nature of these four distributions of weak-spot locations and strengths. This has been done for three cottons which are of commercial interest because of their different behavior in the modified Pressley bundle strength test [1]. One of these, the Hopi Acala 50, has an unusually high Pressley strength in the conventional test, with no space between the clamps. (See Table V.) At a clamp separation of 5 mm. [11], however, it appeared to be no better than the Wilds cotton, although the conventional Pressley rating would indicate it to be far superior. Single-fiber strength tests confirmed the observations of the Pressley test. They also showed that the Wilds differed from the other two in exhibiting higher average strength values for the fibers breaking *at* the reversals than for those fibers breaking *between* reversals.

An examination of the reversal spacing for these cottons showed that the reversals in the Hopi Acala 50 cotton are considerably farther apart than in the other two. Furthermore, the fraction of breaks involving reversals is lower for the Acala cotton by an amount proportional to the number of reversals available to break.

From these data the probable arrangement, shown in Figure 4, of position and strength distributions for the reversals (solid curves) and for the structural defects (dotted curves) has been postulated. The curves in the left half of the figure represent log normal distributions of the distances between weak links in the fiber and are similar to the distribution shown in the right portion of Figure 2. In the interpretation of these curves, the greater the distance between weak links the farther apart they are along the length of the fiber and the lower the number found in any given test length. In the right half of Figure 4 the curves represent simple frequency distributions of the strengths of links in which strength is plotted in a linear manner along the abscissas. Only the relative positions (not shapes) of the curves are significant in the present consideration.

Space does not permit discussion of all the considerations necessary to arrive at this arrangement. Suffice it to point out that it is possible from these distributions to explain in a qualitative way the observed strength relationships of these three varieties of cotton. For example, the high strength which the Hopi Acala 50 gives in the conventional Pressley test, with no space between the clamps, is very probably due to the much lower chance of finding either reversals or structural defects in so short a length of fiber. The Sak cotton has so many more weak places per unit length that even their relatively high strength fails to place it above the Acala on a Pressley scale. On the other hand, the strengths of the weakest links in the Acala cotton are so low that whenever the test is made with a relatively long specimen length this cotton appears much weaker than the Sak.

The Wilds cotton has the most reversals per unit fiber length of the three cottons compared. But because the reversals are relatively stronger than those of the Acala, the Wilds appears to be just as strong in a long test length. In a short test length, the high frequency of weak places makes it appear to be weaker than the Acala.

The experiments herein reported suggest several lines for future work, some of which are now under investigation. The true nature of the distributions of breaking stress for the two types of weakest link-

ages is of considerable interest in the theory of fiber strength. Evaluation of the effect of specimen length on the difference between the mean breaking stresses for the two types of breaks should yield some information in this direction. The effect of moisture on the breaking stresses should be investigated for varieties of cotton other than the Empire cotton observed herein. It may be that this same type of selective action occurs for various chemical treatments which modify fiber strength as well as the fraction of fibers breaking for any one type of break.

Summary

It has been demonstrated that cotton fibers tend to break preferentially at the structural reversals, which may be readily seen when the fiber is placed in a polarizing microscope using elliptically polarized light. The cellulose at the reversals appears to be somewhat more highly crystalline than the cellulose in the remainder of the fiber. It is suggested that the reversals behave as weak places because of internal stresses produced there during the growth and production of the fiber. There are also other points of weakness in the fiber which are probably due to real structural defects in the fiber wall. The observed strength of the fiber under given conditions of test is then a function of the probability factors controlling the location and strength of the weakest link in the tested length, whether that link be a structural reversal or a structural defect of some kind between the reversals. The nature of these probability factors for three commercial cottons has been considered.

Acknowledgments

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Accessibility of Cellulose by Formic Acid Esterification*

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UNSUBSTITUTED CELLULOSES, such as cotton and viscose rayon, are generally believed to have network structures in which submicroscopic crystallites are linked together by somewhat disordered segments of cellulose molecules. The proportions of crystalline and noncrystalline cellulose in a material have logically been expected to influence the properties and behavior of the material. Many independent investigations have therefore been directed to the determination of degree of crystallinity of various celluloses [1, 2, 3, 5, 6, 7, 8, 11, 14, 15, 16].

These investigations have yielded widely divergent results and conclusions. In general, estimates of degree of crystallinity obtained by physical methods are considerably lower than those obtained by chemical methods. This is true particularly of x-ray diffraction as contrasted with acid-hydrolysis methods. The differences in results derived by these two methods have led some investigators to conclude that recrystallization of cellulose may occur during acid hydrolysis.

The recrystallization hypothesis seems reasonable enough. The basis of the acid-hydrolysis method is that the inter-crystalline chain network is chemically more reactive than inaccessible cellulose in crystallites. Consequently, the disordered chain segments are the most rapidly attacked by the acid, and the amounts of noncrystalline cellulose can be estimated from rates of hydrolysis. The proponents of recrystallization argue that cutting of the inter-crystalline chain segments removes restraints and allows the loose chain ends freedom to undergo crystallization. Thus, as more and more chains are cut, more and more crystallization occurs, and the final estimate of crystallinity is considerably higher than the true value for the intact sample.

Recrystallization alone may not be extensive enough to account for the large differences between x-ray and hydrolysis estimates of crystallinity. It is apparent that the cellulose is in an aqueous medium throughout the hydrolysis and that aqueous swelling effects should oppose crystallization. For example, it is well known that newly formed cellulosic fibers are but little crystallized prior to their first real drying-out.

Hermans and Weidinger [9], who recently reported some x-ray studies, have been especially critical of the acid-hydrolysis method. They expressed the opinion that chemical methods for determining degree of crystallinity are, *a priori*, likely to give results of dubious physical significance; their x-ray methods demonstrate that acid hydrolysis is particularly bad in this respect because the degree of crystallinity may be altered by the reaction itself.

It is probably unwarranted to assume that degree of crystallinity can, in the strictest sense, be determined by chemical methods. X-ray methods are ideal for the study of perfectly ordered, intact crystals, and perhaps can also be used for estimating degree of crystallinity, but not entirely without error. On the other hand, it is unreasonable to assume that estimates based on chemical methods are meaningless, particularly if part of the structure is not crystalline in the x-ray sense but is, nevertheless, well enough ordered to behave like crystalline substance.

There appears to be a real need for a definition of terms. In much common practice the degree of crystallinity as such is not of major importance; the really significant factor is the amount of reactive cellulose. For example, the swelling of cellulose in water is largely, if not wholly, the result of imbibition of water by noncrystalline cellulose. All aqueous processes, such as dyeing, pulping, degradation, and certain types of resin finishing, and all moisture-sensitive fibers properties, such as plasticity, strength, and elongation, are dependent upon that fraction of the structure to which water gains access. The term "accessible" is applied to this fraction.

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It is a fair assumption that, for practical purposes, a division of the cellulose structure into accessible and inaccessible fractions is more realistic than a division into crystalline and noncrystalline fractions. Furthermore, this division into active and inactive fractions can undoubtedly best be made by chemical methods, which depend upon reactivity.

The formic acid esterification method used in the present investigation has an important advantage over the hydrolysis method. As is shown later, little, if any, cutting of primary valences takes place in this method, and consequently the danger of recrystallization is ruled out. It has the further advantage of being a chemical method.

The method is comparatively simple, requires no specialized equipment or chemicals, and yields data which can be interpreted in a straightforward manner. Unsubstituted cellulose is merely esterified under controlled conditions with strong formic acid and the amount of combined formic acid is determined by saponification of the treated cellulose.

Experimental Procedure and Results

The esterification of cellulose with formic acid has been reviewed briefly by Malm and Fordyce [12] and by Heuser [10]. The former assert that 6%–10% of formyl groups can be introduced readily into cellulose by treatment of the material at room temperature with formic acid of at least 85% strength. Heuser stated that formic acid simultaneously esterifies and degrades cellulose and that degradation occurs particularly where the cellulose monoformate stage is exceeded. Both reviews indicate that cellulose formates are unstable, are readily hydrolyzed by hot water, show a strong tendency to hydrolyze at room temperature in the presence of moisture, and are completely stripped of formyl groups by dry heat at elevated temperatures. Heuser's review also indicates that the introduction of more than one formyl group per glucose unit is difficult and that cellulose triformate cannot be isolated.

Preliminary experiments were undertaken to determine what precautions would have to be taken in the handling of formylated samples. A few experiments quickly established the fact that esterification of cellulose at room temperature with 90% formic acid reagent yields reproducible saponification data.

The heat and moisture stabilities of partially formylated cellulose were then investigated. Swatches of cotton and viscose rayon fabrics were soaked together for 20 hrs. in an excess of 90% formic acid at room temperature. The swatches were then removed and rinsed in cold running water for 30 min. This rinsing was continued somewhat longer than was necessary to leave the samples neutral to methyl orange. The wet samples were then torn in half and one part of each was dried at room temperature. The other part of each was dried in a forced-circulation air oven at 300°F for 1 hr. Analysis by saponification yielded the data in Table I.

These data clearly show that the partially formylated celluloses are stable enough toward heat and moisture to permit ordinary oven-drying and handling without danger of formyl losses.

It was next shown that little cutting of chains occurs during partial formylation. The strength of cotton is highly sensitive to acid degradation and offers a ready means of determining appreciable acid damage. Accordingly, a piece of bleached, pure-finish cotton sheeting was soaked for 18 hrs. in 90% formic acid at room temperature. The cloth was then removed, rinsed thoroughly in running water, and dried. After being conditioned at 70°F and 65% R.H., pieces of formylated and untreated control fabrics were tested for breaking strength by the A.S.T.M. cut-strip method. The observed data are shown in Table II.

These results indicate that the amount of cellulose degradation is inappreciable in periods up to 24 hrs. at least.

The modified Eberstadt saponification technic [13] for determining degree of esterification is widely used

TABLE I. HEAT STABILITY OF CELLULOSE FORMATE

Sample and treatment	Combined formic acid (%)
Formylated cotton—unheated	5.76
Formylated cotton—heated 1 hr. at 300°F	5.60
Formylated viscose rayon—unheated	19.1
Formylated viscose rayon—heated 1 hr. at 300°F	19.0

TABLE II. EFFECT OF PARTIAL FORMYLATION ON STRENGTH OF COTTON

	Combined formic acid (%)	Breaking strength (lbs.)	
		Warp*	Filling*
Untreated control	0	68.4	58.4
Sample formylated 18 hrs.	4.9	68.2	60.0

* Values given are the averages of 5 determinations.

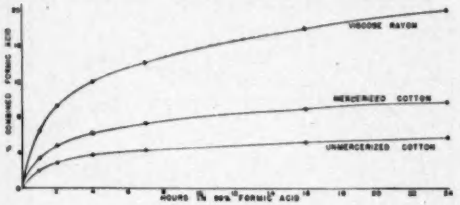

FIG. 1. *Simultaneous formylation results for viscose rayon, mercerized cotton, and unmercerized cotton at 30°C.*

and is reasonably accurate and reliable. It has therefore been assumed to be adequate for present purposes without change.

Typical formylation results for three different cellulosic materials are presented graphically in Figure 1. Unmercerized, bleached cotton print cloth; mercerized, bleached cotton print cloth; and an all-spun, all-viscose rayon were simultaneously formylated at 30°C for varying times. The mercerized cotton was prepared from the unmercerized print cloth by immersion of the latter without tension in 23% caustic at room temperature, rinsing thoroughly, souring, and drying. All samples were in pure-finish form.

Swatches of each of the three types of fabric were tacked loosely together with cotton thread. Of seven such sets made, six were placed in 1 l. of 90% formic acid at 30°C. Sets were removed periodically up to 24 hrs., rinsed in cold running water for 30 min. immediately after removal, and air-dried. The sets were subsequently broken; the individual samples

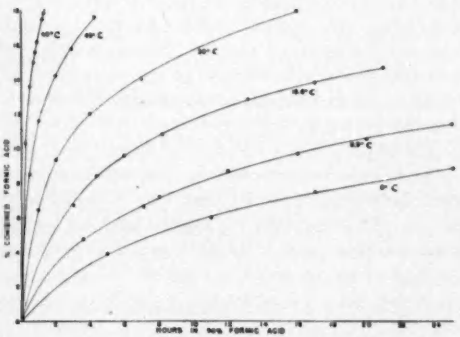

FIG. 2. *Effect of temperature on the formylation of viscose rayon.*

were oven-dried for 1 hr. at 105°C and saponified with excess 0.25*N* NaOH for 24 hrs. at room temperature.

The curves clearly show that viscose rayon esterifies to a greater extent than does mercerized cotton, which, in turn, undergoes more esterification than unmercerized cotton does. In all cases the esterification is initially rapid but proceeds at a decreasing rate which ultimately tends to become constant. The shapes and pattern of the curves are strongly suggestive of acid-hydrolysis curves.

The esterification process is visibly similar in the three cases. Actually, ratios both of simultaneous values for viscose rayon and for mercerized cotton to those for unmercerized cotton vary but little over the 24-hr. period. The viscose rayon-unmercerized cotton ratios increase linearly from 3.1 to 3.5 in 24 hrs., while the mercerized-unmercerized cotton ratios increase linearly from 1.6 to 1.7 in the same period.

The effect of temperature on the esterification of viscose rayon with 90% formic acid is shown in Figure 2. Values of combined formic acid were obtained by the methods already described. The graph indicates that the esterification process is much accelerated by heat. However, the process is not otherwise changed since the curves coincide when the time scales are adjusted by appropriate factors.

The relative velocities of esterification at different temperatures were determined and the energy of activation was calculated. Relative reaction velocities were found by taking the reciprocals of the times required for the same amount of formic acid to be combined at the various temperatures. The activation energy, calculated from these relative velocities, is approximately 14,000 cals.

Activation energy, E, is given by the equation

$$E = \frac{4.606 \log \left(\frac{h_2}{h_1} \right)}{\frac{1}{T_1} - \frac{1}{T_2}},$$

where h_1 and h_2 are times required for the same amount of formic acid to be combined at two different temperatures, T_1 and T_2, respectively, expressed in °K.

The interpretation of cellulose-esterification data presented another problem. The amounts of cellulose involved in the esterification are obviously dependent upon the product formed—whether the mono-, di-, or tri-ester, or mixtures of these types.

TABLE III. FORMYLATION OF STARCHES AND DEXTRIN (90% FORMIC ACID AT 21°C FOR 4 HRS.; SAMPLES RUN IN PARALLEL)

Material	Combined formic acid (%)
Corn starch	23.3
Potato starch	23.3
Arrowroot flour	23.0
Brazilian tapioca	23.0
White dextrin	23.5

Each glucose unit of cellulose contains a primary and two secondary hydroxyls, which might esterify at different rates.

A preliminary experiment was conducted to determine whether primary and secondary hydroxyls formylate at grossly different velocities. Normal and secondary butyl alcohols were mixed with excess 90% formic acid. Periodic dilution of portions of these mixtures with water showed that insoluble butyl formates were formed in a few minutes at room temperature in both cases. This result indicated that both the primary and secondary hydroxyls of cellulose might be involved.

The next step was to investigate the esterification behavior of a completely accessible material. Starches are known to be practically identical to cellulose in chemical composition and to form opalescent solutions readily in 90% formic acid at room temperature. White dextrin reagent forms a water-white solution under the same conditions. The latter was obviously ideal, provided its chain length was not so short that end groups would introduce an interfering factor.

Four different starches and white dextrin were dried *in vacuo* at room temperature and esterified in parallel for 4 hrs. at 21°C. Portions of the same formic acid were used for each sample. Approximately 1.8 g. of the dry starches and dextrin were placed in flasks with 50 ml. of 90% formic acid. The flasks were stoppered and rotated until dispersion was complete. At the end of 4 hrs. the reaction was quenched by addition of 200 ml. of chilled methanol to each flask. The precipitates which formed were filtered off, washed several times with methanol, dried *in vacuo*, and subsequently saponified.

The data obtained are given in Table III.

The similarity in reaction behavior of starch and dextrin is also apparent in Figure 3, which depicts the formylation of Brazilian tapioca and white dextrin for a 72-hr. period. One formyl group per glucose unit corresponds to 24.2% combined formic. The curve, then, suggests that one hydroxyl per glucose unit is formylated rapidly. Simultaneously, but far more slowly, esterification of one or both of the remaining hydroxyls apparently occurs. This is represented by the flattened portion of the curve and the dotted projection to 24.2% combined formic acid.

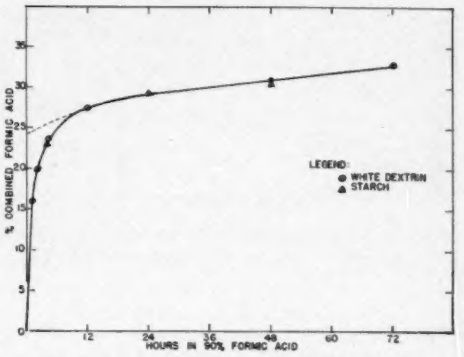

FIG. 3. *Formylation of starch and dextrin at 21°C.*

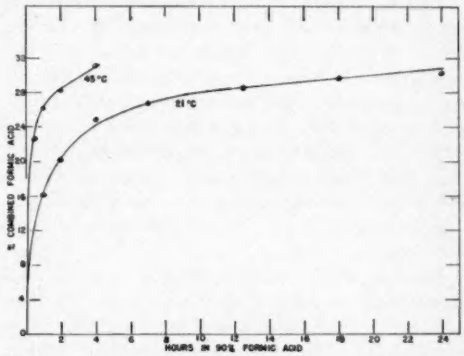

FIG. 4. *Effect of temperature on the formylation of white dextrin.*

The effect of temperature on the esterification of white dextrin is shown by Figure 4. Calculation of the activation energy by the method used for viscose rayon yields a value of 14,200 cals. This is almost identical to the value for viscose and is strong evidence that the same process is involved in the two cases.

The information obtained in these experiments served as the basis on which white dextrin was

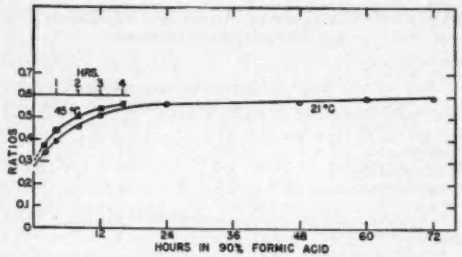

FIG. 5. *Simultaneous ratios of combined formic acid in viscose rayon to that in dextrin.*

chosen to represent 100% accessibility. On the assumption that esterifications of dextrin and cellulose are identical chemical processes, the simultaneous ratios of formic acid values for viscose rayon to those for dextrin were calculated; these are plotted in Figure 5. Thus, each point on the graphs represents the amount of combined formic acid in viscose rayon relative to that in white dextrin for the same time-temperature conditions of formylation for each.

The series of ratios for 21°C indicate that the esterification of viscose rayon differs progressively in time from that of dextrin.* In other words, at the start of the process about 0.3 as much formic acid combines with viscose as combines with dextrin. This ratio increases relatively rapidly with time at a decreasing rate and finally settles to a slow, steady rise after about 24 hrs. In the 45°C series, the initial ratio is again in the vicinity of 0.3, but rises more rapidly and approaches a slow rate of change in 4 hrs. The 24-hr. value at 21°C and the 4-hr. value at 45°C are almost identical.

The curves can be given at least one simple interpretation—that viscose rayon is initially about 30% accessible to 90% formic acid. As esterification proceeds, the amount of accessible cellulose increases, but at a decreasing rate. The rate finally becomes slow and constant when about 55% of the viscose has become accessible. It is suggested, therefore, that the viscose rayon examined is initially about 30% accessible to 90% formic acid, that an additional 25% becomes accessible in 24 hrs., and that the remaining 45% is but slowly attacked and may be inaccessible crystalline or near-crystalline material. It is interesting to note that both 21°C and 45°C curves appear to extrapolate to about 30%.

TABLE IV. ESTIMATES OF ACCESSIBLE CELLULOSE FROM EXTRAPOLATION OF SIMULTANEOUS RATIOS OF COMBINED FORMIC ACID IN CELLULOSIC MATERIAL TO COMBINED FORMIC ACID IN DEXTRIN

Cellulosic material	Accessible cellulose (%)
Viscose rayon	28–30
Mercerized cotton	14–15
Unmercerized cotton	8–9

Similar handling of unmercerized cotton and mercerized cotton data gave the initial accessibilities shown in Table IV. The value for viscose rayon is included.

It is emphasized that these values are estimates of cellulose *initially accessible to 90% formic acid*. Formic acid of this strength is a more powerful swelling agent than is water. The percentages of these celluloses immediately accessible to water would therefore be somewhat lower than the values given. If the above concept is correct, then a considerable part of each of these structures is not immediately accessible to water but nevertheless does not act as if it were crystalline. Furthermore, water cannot increase the accessibility of this intermediate structure by chemically reacting with it as formic acid can. However, it is a distinct possibility that at least some of this intermediate structure may be made accessible to water by mechanical action, such as the beating of a pulp, or by chemical action, such as by dilute alkali, aqueous urea, and dicyandiamide solutions.

That a part of the viscose rayon structure may gradually become accessible to formic acid as esterification takes place can be inferred from Figure 6. This graph shows the esterification of viscose rayon fabric by formic acid reagent over a period of a week.

Except for the first 24 hrs., the reaction proceeds at a slow, steady pace. However, after about 40 hrs. the fabric obviously begins to disintegrate. The disintegration is unquestionably the result of partial

* The simultaneous ratios of percentages of combined formic acid in cellulose to those for dextrin are only approximations of the amounts of cellulose actually esterified. The relative amounts of cellulose esterified are given more accurately by simultaneous ratios of moles of combined formic acid per mole of anhydroglucose in cellulose and in dextrin. Thus, where the simultaneous percentages of combined formic acid in cellulose and in dextrin are A_C and A_D, respectively, the *approximate* amounts of cellulose esterified are given by the ratio $\frac{A_C}{A_D}$. More accurate estimates of cellulose esterified, based on moles of combined formic, are given by $\frac{A_C}{A_D}\left[\frac{4600-28A_D}{4600-28A_C}\right]$. However, the correction factor represented by the quantity in the brackets is neglected as an unnecessary complication of the present discussion.

solution of the viscose rayon since dilution of the clear supernatant formic acid with methanol produced a precipitate in the form of a distinct turbidity. This indicates that 90% formic acid is a solvent for formylated cellulose. Thus, the solvent action of 90% formic acid on formylated chain segments of accessible cellulose could presumably expose additional cellulose to the esterifying agent. This effect would explain the slow erosion of crystalline cellulose as well as the relatively rapid change of accessibility with time in the early stages of the process.

Direct evidence that formic acid does not enter cellulose crystallites was obtained from x-ray diffraction analysis of partially formylated cotton and viscose rayon. Samples of these materials as fabrics were treated with 90% formic acid for 40 hrs. at 21°C, rinsed thoroughly, and dried. As can be seen by reference to Figure 6, this time of treatment was not quite long enough to produce incipient disintegration of the viscose rayon. Combined formic acid in the viscose rayon and cotton was 18.7% and 5.0%, respectively.

Threads taken from untreated and formylated samples were examined with Cu $K\alpha$ radiation. Neither optical nor photometric measurements of the diffraction patterns indicated that any change in the crystal lattice spacing had occurred as a result of the formylation. A change in the lattice spacing would probably occur if formic acid entered the crystallites.

A less laborious, but also less accurate method than that described above can be used to resolve formylation data. This consists simply of determining two sample-dextrin ratios—one near the origin of the curve in Figure 5, and one in the flattened

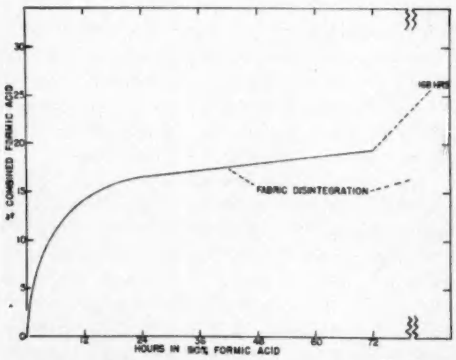

FIG. 6. *Formylation of viscose rayon fabric at 21°C.*

TABLE V. ESTIMATES OF ACCESSIBLE, NONCRYSTALLINE, AND CRYSTALLINE CELLULOSE

Material	Accessible cellulose* (%)	Non-crystalline cellulose† (%)	Crystalline cellulose‡ (%)
Viscose rayon	39	54	46
Mercerized cotton	20	28	72
Unmercerized cotton	12.5	16	84

* Combined formic ratio, material/dextrin, after 2 hrs. at 30°C.

† Combined formic ratio, material/dextrin, after 12 hrs. at 30°C.

‡ By difference.

region. A sample-dextrin ratio at any early stage in the reaction would indicate the initial accessibility only approximately for two reasons: First, if the time of formylation were too short, the ratio would not be reliable because the degrees of formylation might be too small for accurate measurement, and diffusion of reagent into fibers might be a retarding factor. Secondly, if the ratio is taken longer and longer after the outset of reaction, it is increased more and more by cellulose which becomes accessible as the reaction proceeds. Nevertheless, it should be possible by this method to obtain comparable figures on a variety of materials with little expenditure of time.

Sample-dextrin ratios determined after sufficient time has elapsed for the formylation rate to have become slow and constant should be fairly accurate. These ratios, of course, would indicate the amounts of residual inaccessible material in the samples.

The rough analysis of cotton, mercerized cotton, and viscose rayon by use of two sets of ratios is presented in Table V. The percentages of accessible cellulose are derived from material-dextrin ratios after 2 hrs.' formylation of each at 30°C. Noncrystalline cellulose is similarly obtained from the material-dextrin ratios after 12 hrs.' formylation of each at 30°C. The figures for crystalline cellulose are simply the differences between derived percentages of noncrystalline material and 100. The amounts of accessible cellulose in this table are considerably higher than those estimated for the same materials by extrapolation (Table IV). This is to be expected for the reasons given above.

Discussion

The partial formates of cellulose, prepared and heat-treated as described in the preliminary experi-

ments, appear to have relatively good stability. This is clearly a contradiction of the literature on cellulose formates. Nevertheless, it seems likely that the monoformate is relatively stable, and it may well be that substituent formyl groups in excess of the monoformate are relatively unstable, as well as being difficult to introduce [10]. In such a case, the idea could readily have developed that cellulose formates are completely unstable.

Whether or not there is appreciable acid degradation of cellulose during esterification is doubly important. In addition to its bearing on recrystallization of cellulose, chain-cutting would increase the number of hydroxyls available for esterification and, accordingly, would have to be considered in the interpretation of data. The fact that cotton fabric retains its strength through esterification is strong evidence that chain-cutting is inappreciable. Cotton-fabric strength apparently is fully as sensitive a measure of chemical degradation as is cuprammonium fluidity [4], which depends upon chain length.

The absence of acid degradation in the process is also indicated by the behavior of dextrin after prolonged esterification. The partial formates of dextrin on being saponified in dilute caustic yield opalescent solutions which are indistinguishable from solutions of untreated dextrin. Formylated starches also give opalescent dispersions after saponification. These observations suggest that acid degradation occurs at the most only very slowly since neither starch nor dextrin hydrolyzes to completely water-soluble, low-molecular-weight fragments in periods up to 3 days.

Being considerably lower in molecular weight than the starches, dextrin should have shorter chains and hence more terminal (position 4) hydroxyls per unit weight than the starches. If such terminal hydroxyls were preferentially esterified, dextrin should accept more combined formic acid than the starches. However, in parallel esterifications the starches and dextrin do not differ significantly (Table III and Figure 3). Furthermore, if all formyl above that necessary to produce the monoformate were on position-4 hydroxyls, the degree of polymerization of starches and dextrin after 24 hrs. (Figure 3) would have to be 4, and after 72 hrs. slightly more than 2. In view of the opalescence of the regenerated starches and dextrin (discussed above), such low degrees of polymerization are improbable. It follows, therefore, that formyl in excess of that required to produce the monoformate is probably present as the diformate on relatively undegraded chains.*

It is unlikely that appreciable error in the saponification data is caused by solvent action of the 90% formic acid during the esterification process. Such errors would arise if formyl-rich cellulose chain fragments were carried off in the excess of formic acid. However, as has already been mentioned, only a slight amount of such extraction was observed when viscose rayon was formylated for 40 hrs. Thus, only a negligible amount of extraction from viscose rayon could have occurred in experiments run for far shorter times.

In the case of cotton which was formylated for a week there was no evidence whatever of any extraction. Not only does this exclude the likelihood of error from extraction, but it also indicates that extractable chain fragments are not formed by degradation during the long time of treatment. The absence of appreciable extraction, especially in the case of viscose rayon, may stem from the fact that formic acid is not a strong intra-crystalline swelling agent.

The factual data and the inferences drawn from them in the above presentation emphasize the need for precise definition of terms in this field. "Accessibility," for example, cannot be used alone except for generalization. Where measurements are involved, the term must be limited and defined before any significance can be attached to the data. Thus, accessibility to 90% formic acid and accessibility to helium are probably very different values. "Accessibility" obviously cannot be a specific term until the conditions are described.

The accessibility of a cellulose to water is actually of the widest and most practical interest. In fact, the relative crystallinity is clearly secondary to relative accessibility in real significance.

The possible existence of a stratum or strata of potentially accessible cellulose between the immediately accessible and the inaccessible fractions is also of prime, practical importance. It may offer an explanation of some of the large discrepancies in measurement of degrees of crystallinity. Its possible role in the beating of paper pulp, for example, has been mentioned above.

The initial accessibilities of unmercerized and mercerized cottons and of viscose rayon to 90%

* An independent investigation [17] by a different method apparently has led to different conclusions.

formic acid are probably somewhat higher than the accessibilities of these materials to water. Nevertheless, the estimates obtained are in the same ranges as those obtained by acid hydrolysis.

Summary

A method of investigating the structure of unsubstituted celluloses by formic acid esterification is presented.

It is proposed that the degree of accessibility of a cellulose structure to water is a far more useful value than the degree of crystallinity.

Cellulose structures appear to contain three distinct parts: one part is immediately accessible to a contacting medium like water; a second part is potentially accessible; while a third part is inaccessible.

Accessibilities must be described in terms of the swelling power of the contacting medium, which may convert varying amounts of the potentially accessible cellulose to fully accessible cellulose.

The most practically useful data on cellulose structures can probably best be determined by chemical methods.

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On the Mechanism of the Hydrolytic Cleavage of the Interunit Bonds in the Cellulose Molecule

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THE PRESENT STUDY is a consideration of to what degree in the partial, hydrolytic degradation of cellulose the breaking of bonds between glycosidic or monomeric units occurs randomly. It is thus necessary that experimental determination be made, both before and after the hydrolytic treatment of cellulose, of either the number or weight distributions—*i.e.*, so that either the proportional frequency or the weight of molecules of various degrees of polymerization in successive samples of cellulose be determined in the course of the hydrolytic degradation. The present work is concerned with several such distributions in a series of progressive partial degradations reported by Jörgensen [6].

The approach to the problem is that common in current statistical procedure: an assumption is made and then the assumption is judged on the grounds of its inevitable implications. In the present case, it is supposed that the breaking occurs randomly. If this is true, there should exist certain relations between the number distributions before and after degradation. Insofar as such relations exist, it may be supposed that the assumptions are not invalidated.

The principal problem in the present approach is that of specifying the relation between the number distributions before and after degradation. It is suggested that the statistical moments of the two distributions be considered. They provide a convenient and precise solution to the general problem of testing the assumption of random breaking. The use of these moments is the main contribution of the present communication; they might perhaps be more generally employed for testing a variety of hypotheses on the nature and behavior of cellulose.

Review of Theoretical Treatment in the Literature

The primary assumption treated in the present study is that all bonds between monomeric units are equally liable to being broken, regardless of the molecule where they occur or their position within that molecule. This condition can never obtain fully for cellulose because Freudenberg *et al.* [3, 4] showed in a study of cellobiose, cellotriose, cellotetrose, etc., successively, that end bonds break at a very much higher rate than do other bonds. Their work indicated, however, that as the position of a bond becomes remote from the end of the molecule, the chance of a break very rapidly approaches a level common for the remainder of the molecule. Accordingly, even the peculiarities of bonds towards the end of the molecule will be of minor importance in the consideration of material that is fairly highly polymerized, and it is possible that the condition of random disjunction is approached for practical purposes.

Surveys by Mark and Harris [10] and by Jörgensen [6] of various theoretical approaches to the theory of partial degradation show considerable variability partly because in order to simplify mathematical operations they made various arbitrary assumptions as to the nature of the initial distribution. Specific hypotheses that the breaking of bonds is not random, as treated by Jellinek [5] and Schulz [17], are limited by the condition that the initial distribution is supposed quite uniform. Such results can find application only to the degradation of very homogeneous fractions obtained from general samples. The more general case of degradation of chains of finite but varying length, when the bonds break with various probabilities, has been dealt with by Simha [18] and by Debye, whose work is discussed by Mark and Raff [11]. The solutions are, however, highly involved and are of such a nature that it would be difficult to test them in any practical case. In work that is more closely related to the present study—*i.e.*, when the hypothesis was that of random breaking—Kuhn [8, 9] supposed the initial molecules to be of infinite length. Kuhn's reasoning has been followed repeatedly. Schulz [16] subsequently made

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the point that this is only a special form of the case where the initial molecules are of uniform, finite length.

The results of random breaking, when the initial molecules are considered to be of uniform, finite length, has been attacked by Durfee and Kertesz [2], Montroll and Simha [14], Mark and Simha [12], and Sakurada and Okamura [15]. Typically, they find that if λ is the universal initial size of molecules in the untreated material, the frequency of molecules of size $L < \lambda$, by degradation, is

$$F_L = pq^L(\lambda p - Lp - p + 2), \qquad (0 \leq L < \lambda) \tag{1}$$

where F_L is the frequency of molecules of size L relative to the initial size, λ; p is the chance of a bond's being broken; and $q = 1 - p$ is the chance of a bond's surviving. For the undegraded molecules the frequency is

$$F_L = q^L. \qquad (L = \lambda) \tag{2}$$

For the purpose of the present study, the size of a molecule is taken as the number of bonds between monomeric units—not as the number of monomeric units.

Any attempt to generalize the results of equations (1) and (2) from the assumption of uniform initial molecular length to that of initial material of various degrees of polymerization would be very difficult. In general, the frequency of a molecule of size L arising as a result of the disintegration of some larger molecule is

$$F_L = \sum_{\lambda=L+1}^{\infty} pq^L(\lambda p - Lp - p + 2)\phi_\lambda, \qquad (0 \leq L < \lambda) \tag{3}$$

while the probability of its arising without degradation is

$$F_L = q^L\phi_\lambda, \qquad (L = \lambda) \tag{4}$$

where ϕ_λ is the frequency of a molecule of size λ relative to the frequency of all molecules in the initial material. It can be seen that equations (3) and (4) hardly admit of treatment unless ϕ_λ is given functional form.

Following the general line of investigation in this field, Montroll [13] started with the supposition that ϕ_λ, the initial number distribution, should be normal or Gaussian. He arrived at an expression for the change in the average molecular size with partial degradation. This result is itself of very limited value because the necessary condition will probably be approached but rarely. By the device, however, of representing a non-normal distribution as the sum of a series of distributions related to the normal, he was able to extend in a theoretical way the field of application for his results. It is, however, very hard to follow his procedure—he himself did not attempt an application beyond the simple normal case. Further, the method could hardly be extended to embrace distributions where two or more maxima occur in the frequency distribution of the initial material. Such a distribution was shown in the work of Jörgensen [6] for spruce pulp.

Failing a general solution for the situation where the initial material is of various degrees of polymerization, the results for uniform initial size have been widely applied to the degradation of all materials. Generally, as pointed out by Jullander [7], the theoretical result, on such a basis, and the corresponding experimental result have been widely discrepant. Such a discrepancy is to be expected, for the theory can at most be only of practical interest for very well fractionated material; then the fractions may have such a narrow distribution of molecular size that they are effectively homogeneous. When, however, the present theory is applied to the degradation of unfractionated materials—both wood pulps and cotton—the fundamental assumptions are very far indeed from being satisfied. Just how discrepant are the conclusions on such a basis is shown in detail in a later section (page 211).

It may be seen from the above review that there has been devised no general and practical method to check theoretically whether in the partial degradation of cellulosic material the breaking of interunit bonds is random. The principal difficulty seems to have been that workers approached the matter by trying to determine the form of a partially degraded distribution, F_L, from that of the initial distribution, ϕ_λ. Accordingly, they have been vexed by the mathematical form of the initial distribution, both because it is commonly unknown and because if it were known, it would complicate their result. This distribution may, of course, be determined with some exactitude in an empirical way, but it will not, in general, be characterized by

any known mathematical function. In the present study a new approach to this problem is made by carrying on the discussion without any restriction on the form of the distribution of the initial material or that of the partially degraded material. A general solution is provided regardless of the form of the initial distribution.

Relationship Between the Statistical Moments of the Distribution of Molecular Size for Partially Degraded and Initial Cellulose

The present treatment of the problem of degradation is quite general with regard to the mathematical form of the distributions involved, but is, in reiteration, restricted to the hypothesis that the chance of a bond being broken is independent of the length of the chain in which it occurs or its position within that chain—*i.e.*, that the bonds are broken at random. It is proposed to consider, under this hypothesis, the dependence of the statistical moments of the distribution of molecular size in the partially degraded material upon the corresponding moments of the initial material. (The form and meaning of statistical moments are discussed in some detail later. See pp. 205–6.) The mathematical form of the frequency distribution of molecular size which has vexed previous workers seems generally unnecessary and is avoided in the present discussion. Generally, these forms are of no intrinsic importance but are only means to the end of discovering whether the hypothesis under consideration is tenable.

Before proceeding to a general solution, it may be profitable to present a very simple illustration of data of an hypothetical character. These data emphasize the difficulties of the problem and serve to prove any conclusions. It was supposed that the initial material ranged from monomeric units up to cellohexose and that each level of polymerization was represented by equal numbers of molecules. Algebraically, in this very simple initial distribution, $\phi_\lambda = 0.166667$ for all $\lambda = 0$ to 5. It was assumed that the chance of a bond's breaking was $p = 0.1$; and of its surviving, $q = 0.9$. In such a simple illustration the result may be found from the existing theory, although with a little effort; equations (1) and (2) may be employed. The degraded material from each polymer may be found alone and then the total amount may be compounded; the operation is as follows.

Consider first the initial material, the molecules of which were of size $\lambda = 5$ (*i.e.*, with 5 bonds) and the frequency with which molecules of various size will result when these molecules are subjected to degradation. Employing equations (1) and (2), the proportionate frequencies in the final material are found to be:

L	F_L/ϕ_λ
0	0.24000
1	0.20700
2	0.17820
3	0.15309
4	0.13122
5	0.59049

Similar results were obtained for $\lambda = 4$ to 0; these are given in Table I. Since it was now supposed that each of the degraded distributions arose from an initial class comprising $\frac{1}{6}$ of all initial molecules, the total degraded distribution must be the sum of the various degraded distributions, each with a weight of $\frac{1}{6}$ of the total. Using the total distribution for all breaks, for each value of $\lambda = 0$ to 5, one finds the total degraded distribution, as given in Table I and illustrated in Figure 1.

It is evident that the labor involved in calculations of the sort underlying Table I would become very great as the range of λ increases. In short, it would be impossible to study any complex distributions of initial and degraded material by this method.

From the definition of ϕ_λ it follows that

$$\sum_{\lambda=0}^{\infty} \phi_\lambda = 1, \tag{5}$$

but the total for the degraded material,

$$\sum_{L=0}^{\infty} F_L \neq 1. \tag{6}$$

Thus, in Table I, this latter sum is 1.25.

The statistical moments will now be defined. Call the rth ($r = 1, 2, 3, 4, \ldots$) moment of the initial distribution

$$\mu_r = \sum_{\lambda=0}^{\infty} \lambda^r \phi_\lambda. \tag{7}$$

Similarly, the rth moment of the degraded distribution is

$$m_r = \sum_{L=0}^{\infty} L^r F_L \Big/ \sum_{L=0}^{\infty} F_L. \tag{8}$$

TABLE I. THE FREQUENCY OF EACH KIND OF DEGRADED MOLECULE TIMES THE FREQUENCY OF THE INITIAL MOLECULE TO DISCOVER THE TOTAL DISTRIBUTION OF DEGRADED MATERIAL

	Initial size, λ						
	0	1	2	3	4	5	
Initial frequency	0.166667	0.166667	0.166667	0.166667	0.166667	0.166667	
Degraded size			Degraded distribution				Weighted sum
0	1.0	0.2	0.21	0.220	0.2300	0.24000	0.350000
1		0.9	0.18	0.189	0.1980	0.20700	0.279000
2			0.81	0.162	0.1701	0.17820	0.220050
3				0.729	0.1458	0.15309	0.171315
4					0.6561	0.13122	0.131220
5						0.59049	0.098415

The status of moments may, perhaps, be better appreciated if it is pointed out that the first three moments are intimately involved in general estimates of molecular weight, as found in current theory for polymolecular materials like cellulose. These estimates are as follows: the number average, as found by osmotic pressure and end-group determinations; the weight average, as found by equilibrium measurements in the ultracentrifuge, by measurements of light scattering, and by viscosity determinations, when Staudinger's relationship holds; the so-called "z-average," as found by the scale optical method with data from the equilibrium ultracentrifuge.

The above three relations have been discussed by one of the present writers, Beall [1], from the point of view of statistical moments.

Returning to the general equations (7) and (8), the moments m_r are entirely dependent upon the moments μ_r under the hypothesis being tested. Accordingly, it is possible to consider the relationship between the partially degraded material and the initial material in terms of the relationship between the moments. As will be shown, these moments may be found without a definition of the mathematical form of the distributions, ϕ_λ and F_L, involved. Therefore, it is possible to consider the relationship between the partially degraded material and the initial material without a definition of the mathematical form of the distributions. In order to test this hypothesis of random breaking of bonds it is necessary to discover only whether the values m_r behave as they should in view of the values of μ_r. While with the extension of the series m_r an ever increasingly fine specification of the distributions may be made, it is permissible and wise to carry r no higher than circumstances warrant. In fact, it would be reasonable to be satisfied

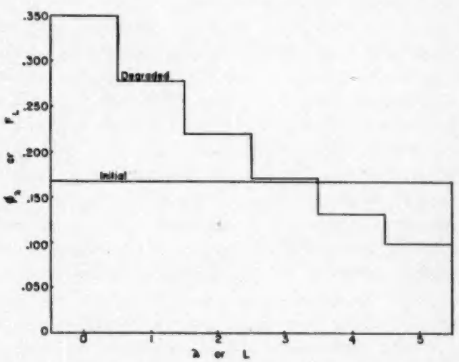

FIG. 1. *Distribution of initial and degraded cellulosic material in the hypothetical example of Table I.*

with correspondence for $r = 2$ and 3, and then assume at least a considerable degree of correspondence between theory and observation.

For the present work, it is not proposed that, in general, the moments be found by physical methods, such as those just discussed. On the contrary, they should be found for any material from the number or weight distributions, which should be first established empirically. It may be noted that if the number distribution is known, its rth moment is

$$\sum_{\lambda=0}^{\infty} (\lambda + 1)^r \phi_\lambda \Big/ \sum_{\lambda=0}^{\infty} \phi_\lambda = \sum_{s=0}^{r} \frac{r!}{s!(r-s)!} \mu_{r-s}. \qquad (9)$$

For practical purposes, when fairly highly polymerized material is involved, equation (9) may be avoided by identifying the rth moment of the number distribution with μ_r. In usual practice, the weight average is found directly (by the use of Staudinger's law and viscosity measurements) and

TABLE II. THE SUMMATIONS $\sum L^r F_L$ NECESSARY FOR THE CALCULATION OF MOMENTS, USING THE DATA OF TABLE I

Size, L	F_L	LF_L	L^2F_L	L^3F_L
0	0.350000	0.000000	0.000000	0.000000
1	0.279000	0.279000	0.279000	0.279000
2	0.220050	0.440100	0.880200	1.760400
3	0.171315	0.513945	1.541835	4.625505
4	0.131220	0.524880	2.099520	8.398080
5	0.098415	0.492075	2.460375	12.301875
$\sum L^r F_L$	1.250000	2.250000	7.260930	27.364860

the weight distribution is found from fractionation experiments. From the distribution curve the number average (or first moment) may be calculated. The number average may also, if the materials possess a medium-high molecular weight, be found from osmotic measurements directly. For the weight distribution—*i.e.*, the proportionate weight of molecules of various degrees of polymerization—the rth moment is

$$\sum_{\lambda=0}^{\infty} (\lambda+1)^{r+1}\phi_\lambda \Big/ \sum_{\lambda=0}^{\infty} (\lambda+1)\phi_\lambda = \sum_{s=0}^{r+1} \frac{(r+1)!}{s!(r+1-s)!}\mu_{r+1-s} \Big/ (\mu_1+1). \quad (10)$$

Again, for practical purposes, equation (10) may be avoided by identifying the rth moment of the weight distribution with μ_{r+1}. Thus, values of μ_r may be established from data normally collected from experimental work on fractionation, without any question as to the mathematical form of the distributions involved. The actual details of such operations are discussed at some length in the following section (page 210) on illustrative application of the present theory.

The procedure for the calculation of moments is illustrated in Table II using the data of Table I for the degraded distribution. The necessary summations, $\sum L^r F_L$, are shown in Table II. These are employed in equation (8) to give moments—*e.g.*,

$$m_1 = \sum_{L=0}^{\infty} LF_L \Big/ \sum_{L=0}^{\infty} F_L = 2.25/1.25 = 1.8. \quad (11)$$

In order to test the hypothesis of random failure of links, it is necessary to develop the dependence of the moments, m_r, of the degraded distribution upon those, μ_r, of the initial distribution.

Consider, first, the probability of a degraded molecule of size L when there occurs a given number, t, of breaks in a molecule of size λ. Consider, in particular, the probability that the last or $(t+1)$th fragment of the original molecule is of size L. Then the previous part of the molecule will comprise $\lambda - L - 1$ bonds including $t-1$ that must fail. These failures can occur in

$$\frac{(\lambda-L-1)!}{(t-1)!(\lambda-L-t)!}$$

equally probable ways, as can be appreciated readily from consideration of the coefficient of the tth term of the expansion of $(q+p)^{\lambda-L-1}$. Accordingly, the probability that the $(t+1)$th fragment is of size L is

$$\frac{(\lambda-L-1)!}{(t-1)!(\lambda-L-t)!} q^\lambda \left(\frac{p}{q}\right)^t.$$

Since the breaking of bonds is assumed to be random, one degraded molecule is as likely to be of a given size as is any of the other molecules. Specifically, the chance of the $(t+1)$th fragment being of magnitude L is the same as that of any other fragment being of that magnitude. Accordingly, in the breakdown of the initial molecule there must be generated $t+1$ times as many molecules of size L altogether, as is the case when only the last fragment is considered—*viz.*,

$$F_{\lambda tL} = \frac{(t+1)(\lambda-L-1)!}{(t-1)!(\lambda-L-t)!} q^\lambda \left(\frac{p}{q}\right)^t. \quad (12)$$

In connection with the accumulations necessary to find moments of the degraded distribution, one may, from equation (12), write

$$\sum_{L=0}^{\infty} L^r F_L = \sum_{\lambda=0}^{\infty} \phi_\lambda \sum_{t=0}^{\lambda} (t+1) \times \sum_{L=0}^{\lambda-t} \frac{(\lambda-L-1)!}{(t-1)!(\lambda-L-t)!} L^r q^\lambda \left(\frac{p}{q}\right)^t. \quad (13)$$

By substituting successively $r = 0, 1, 2, 3$, etc., it is possible to get the quantities necessary in equation (8) for finding the moments of the degraded distribution. The only problem is that of simplification.

Consider, in equation (13), the case of $r = 0$—*i.e.*, of

$$\sum_{L=0}^{\infty} F_L = \sum_{\lambda=0}^{\infty} \phi_\lambda \sum_{t=0}^{\lambda} (t+1) \times \sum_{L=0}^{\lambda-t} \frac{(\lambda - L - 1)!}{(t-1)!(\lambda - L - t)!} \left(\frac{p}{q}\right)^t q^\lambda$$

$$= \sum_{\lambda=0}^{\infty} \phi_\lambda \sum_{t=0}^{\lambda} (t+1) \frac{\lambda!}{t!(\lambda - t)!} \left(\frac{p}{q}\right)^t q^\lambda$$

$$= \sum_{\lambda=0}^{\infty} \left[\sum_{t=0}^{\lambda} \frac{\lambda!}{t!(\lambda - t)!} \left(\frac{p}{q}\right)^t q^\lambda + p\lambda \sum_{t=0}^{\lambda} \frac{(\lambda - 1)!}{(t-1)!(\lambda - t)!} \left(\frac{p}{q}\right)^{t-1} q^{\lambda-1} \right] \phi_\lambda$$

$$= \sum_{\lambda=0}^{\infty} \phi_\lambda + p \sum_{\lambda=0}^{\infty} \lambda \phi_\lambda$$

$$= 1 + p\mu_1. \tag{14}$$

Consider next, in equation (13), the case of $r = 1$—*i.e.*, of

$$\sum_{L=0}^{\infty} LF_L = \sum_{\lambda=0}^{\infty} \phi_\lambda \sum_{t=0}^{\lambda} (t+1) \times \sum_{L=0}^{\lambda-t} \frac{(\lambda - L - 1)!}{(t-1)!(\lambda - L - t)!} L \left(\frac{p}{q}\right)^t q^\lambda$$

$$= \sum_{\lambda=0}^{\infty} \phi_\lambda \sum_{t=0}^{\lambda} (t+1) \times \left[-t \sum_{L=0}^{\lambda-t} \frac{(\lambda - L - 1)!}{t!(\lambda - L - t - 1)!} + (\lambda - t) \times \sum_{L=0}^{\lambda-t} \frac{(\lambda - L - 1)!}{(t-1)!(\lambda - L - t)!} \right] \left(\frac{p}{q}\right)^t q^\lambda$$

$$= q \sum_{\lambda=0}^{\infty} \lambda \phi_\lambda \sum_{t=0}^{\lambda} \frac{(\lambda - 1)!}{t!(\lambda - t - 1)!} \left(\frac{p}{q}\right)^t q^{\lambda-1}$$

$$= q \sum_{\lambda=0}^{\infty} \lambda \phi_\lambda$$

$$= q\mu_1. \tag{15}$$

By similar but more extended operations for $r = 2$:

$$\sum_{L=0}^{\infty} L^2 F_L = \frac{1}{p^2} \sum_{\lambda=0}^{\infty} \left[q(1-q^2)\lambda + 2q^2 \left\{ z\lambda + \frac{z^2\lambda^2}{2!} + \frac{z^3\lambda^3}{3!} + \frac{z^4\lambda^4}{4!} + \ldots \right\} \right] \phi_\lambda$$

$$= \frac{q}{p^2}(1-q^2)\mu_1 + \frac{2q^2}{p^2} \left(z\mu_1 + \frac{z^2}{2!}\mu_2 + \frac{z^3}{3!}\mu_3 + \frac{z^4}{4!}\mu_4 + \ldots \right), \tag{16}$$

where $z = \log_e q$.

Finally, in the case of $r = 3$:

$$\sum_{L=0}^{\infty} L^3 F_L = \frac{q}{p^2}(1 + 4q + q^2)\mu_1 + \frac{6q^2}{p^3} \left[\{(1-q) + (1+q)z\}\mu_1 + \{(1-q)z + (1+q)z^2/2!\}\mu_2 + \{(1-q)z^2/2! + (1+q)z^3/3!\}\mu_3 + \ldots \right]. \tag{17}$$

The moments m_r, as in equation (8), for the degraded distribution may be found in terms of the moments of the initial distribution from the values of $\sum L^r F_L$ for $r = 0$, 1, 2, and 3, as in equations (14), (15), (16), and (17). The first three moments are:

$$m_1 = q\mu_1(1 + p\mu_1)^{-1} \tag{18}$$

$$\left.\begin{aligned} m_2 &= (1 + p\mu_1)^{-1} \left[\frac{q}{p^2}(1-q^2)\mu_1 + \frac{2q^2}{p^2} \left(z\mu_1 + \frac{z^2}{2!}\mu_2 + \frac{z^3}{3!}\mu_3 + \frac{z^4}{4!}\mu_4 + \ldots \right) \right] \\ m_3 &= (1 + p\mu_1)^{-1} \frac{q}{p^2}(1 + 4q + q^2)\mu_1 + (1 + p\mu_1)^{-1} \frac{6q^2}{p^3} \left[\{(1-q) + (1+q)z\}\mu_1 + \left\{ (1-q)z + (1+q)\frac{z^2}{2!} \right\} \mu_2 + \ldots \right]. \end{aligned}\right\} \tag{19}$$

The second and third moments simplify considerably under practical conditions, where, effectively,

$$p \to 0, \tag{20}$$

as must be the case. Certainly, p will fall far below the value of 0.1 used in the hypothetical example, as may be appreciated from the consideration of the extent of degradation shown in Figure 1.

Under condition (20),

$$z = \log q \to q - 1, \tag{21}$$

when, from equation (19),

$$\begin{aligned} m_2 &\to (1 + p\mu_1)^{-1}\left\{q\mu_1 + q^2\mu_2 - \frac{2}{3!}pq^2\mu_3 \right. \\ &\qquad \left. + \frac{2}{4!}p^2q^2\mu_4 - \frac{2}{5!}p^3q^2\mu_5 + \cdots\right\} \\ m_3 &\to (1 + p\mu_1)^{-1}\left[\frac{q}{p}(1 + 5q)\mu_1 \right. \\ &\qquad + 6q^2\left\{-\frac{1}{2}\mu_2 + \frac{2 - q}{3!}\mu_3 - p\frac{3 - q}{4!}\mu_4 \right. \\ &\qquad \left.\left. + p^2\frac{4 - q}{5!}\mu_5 - \cdots\right\}\right]. \end{aligned} \tag{22}$$

It may be observed that the series of equation (22) will be commonly convergent and probably becomes so rapidly. The approximate nature of relations (22) is dependent upon the approach of p to 0. If, however, there is any question of applicability, relations independent of this condition are given in equation (19). In equation (22), the moments m_r of the degraded distribution have only been defined up to the third moment; more could be found similarly if they should seem necessary.

In an actual experiment the value of p would be unknown but could be found from equation (18):

$$p = (\mu_1 - m_1)/\mu_1(m_1 + 1). \tag{23}$$

It will be appreciated that equation (23) involves only the first moment of the degraded distribution. Employing the estimate of p from equation (23) and moments μ_r of the initial material, it is possible to calculate the second moment, m_2, and third, m_3, of the degraded distribution from equation (22). Then, by comparing these results with the corresponding experimental determinations, it is possible to discover whether the common primary assumption of random breaking with equal probability is tenable. Close correspondence of the second and third moments as calculated from the present theory to the moments found experimentally may be taken as an indication that the hypothesis is tenable.

The exactitude of the present theoretical conclusions may be tested in a practical way by using the hypothetical data of Table I. The moments for the initial material are required:

$$\begin{aligned} \mu_1 &= 2.500000 & \mu_5 &= 737.5000 \\ \mu_2 &= 9.166667 & \mu_6 &= 3{,}419.167 \\ \mu_3 &= 37.50000 & \mu_7 &= 16{,}137.50 \\ \mu_4 &= 163.1667 & \mu_8 &= 77{,}163.17 \end{aligned} \tag{24}$$

The first three moments of the degraded material are:

$$\begin{aligned} m_1 &= 1.800000 \\ m_2 &= 5.808744 \\ m_3 &= 21.89189 \end{aligned} \tag{25}$$

Employing the appropriate values from equations (24) and (25) in equation (23):

$$\begin{aligned} p &= \{2.5 - 1.8\}/\{2.5(1.8 + 1.0)\} \\ &= 0.1 \end{aligned} \tag{26}$$

One may then proceed to obtain m_2 and m_3 from equation (22). In the present case, when the values of m_2 and m_3 are calculated in a manner analogous to that of equation (22), on the basis of the values in equations (24) and (26), it may be found that the values in equation (25) are reproduced. Equation (22) is replaced by the appropriate exact equation (19) because p is very different from zero for the present hypothetical example.

The treatment here proposed is superior to that of Montroll [13] in that the results are not in any way restricted by the condition that the initial number distribution be near the normal or Gaussian form. The operations required for testing the hypothesis involve only the calculation of a relatively simple series. It may be objected that the purpose of such a theory as that of Montroll is more than the testing of hypotheses—thus, it may be required to form some idea of the character or, say, performance of degraded material. This is true. It may be seriously questioned, however, whether any characterization of a distribution will be as apt as that of a short series of moments.

Consider now the situation where the initial material is uniform. In this case the dependence of the moments of degraded material upon those of the initial material may be rewritten from previous results. If the initial material is all of molecules of size λ, then $\mu_r = \lambda^r$. Hence, from equation (18):

$$m_1 = (1 + \lambda p)^{-1}\lambda q \tag{27}$$

It follows that:

$$p = \{\lambda - m_1\}/\{\lambda(m_1 + 1)\}. \tag{28}$$

The relationship of equation (22) is paralleled by

$$m_2 = \left\{ \frac{q}{p}(1+q)\lambda - 2\left(\frac{q}{p}\right)^2(1-q^\lambda)\right\}/(1+\lambda q) \quad (29)$$

$$m_3 = \left\{ \frac{q}{p^2}(1+4q+q^2+6q^{\lambda+1})\lambda - 6\frac{q^2}{p^3}(1+q)(1-q^\lambda)\right\}/(1+\lambda q). \quad (30)$$

Test of the Hypothesis of Random Disjunction Using Experimental Data

The hypothesis of random disjunction of the cellulose molecule in the course of degradation is tested using the data of Jörgensen [6]. The test consists of determining whether the first three moments of a degraded distribution are such as would be anticipated, along the lines developed in the preceding section, from the moments of an initial distribution. The results obtained using previously existing theory—on an assumption of initially uniform material—are contrasted.

The data that are used to test the theory arise from the continuous degradation, in both homogeneous and heterogeneous systems, of cotton, spruce, and aspen cellulose, respectively. In each of the six tests a determination of the degree of polymerization was made from time to time. The polymerization was studied by making a series of very fine fractionations, by successive precipitation and then establishing a weight distribution according to the method discussed by Mark and Raff [11]. The procedure has been published in detail by Jörgensen [6].

A series of such studies of progressive degradation was made, for instance, in the homogeneous degradation of cotton cellulose; a determination was made as soon as the material had been dissolved, another after 50 hrs. of treatment, a third after 150 hrs. of treatment, and a final determination after 400 hrs. of treatment. The homogeneous degradation took place in cellulosic material dissolved in 72% H_3PO_4 at 25° C. The heterogeneous degradation was effected by a solution of $M/2$ $KHSO_4$ at 48° C. The spruce pulp had been produced by the Mitscherlich process. The aspen pulp had been produced by the semichemical process; *A-W* refers here to cellulose in aspen wood isolated as the nitrate by direct nitration.

In order to apply equations (22) and (23) to the experimental weight distributions under consideration, it was first necessary to calculate two moments for the degraded material and a longer series for the initial material. These might be calculated in a simple numerical fashion. The distributions are, of course, far too extensive to permit detailed tabulation like that of Table II—*i.e.*, by unit increments in L, or in λ. By the type of operation usual in statistical work it would, however, be possible to group L, or λ, into broad classes and carry out the operations. While these numerical operations would be possible for the present data, they were, in fact, avoided and replaced by graphic methods, thanks to equipment available at The Institute of Paper Chemistry, Appleton, Wisconsin. This equipment was built by Van den Akker [19] for the mechanical integration of the product of two continuous functions of a common variable. It will be realized that when the value of, say, λ extends over hundreds, ϕ_λ approaches a continuous function, which is to be multiplied by the function λ^r, as in equation (7). Accordingly, the summations $\sum\lambda^r\phi_\lambda$ can be found on the integrator very conveniently. In this way the first through sixth moments were determined for each of 23 treatment distributions.

The procedure used with the experimental data is exactly that indicated in the preceding section for the hypothetical experiment discussed there. The quantity p was estimated from the molecular weights of the initial and degraded distributions, by equation (23), and the values of m_2 and m_3, as calculated from equation (22), were then compared with the corresponding empirical moments of the degraded product. When it was used for some of the degradations of Table III, equation (22) was so rapidly convergent that the six moments, as found, were sufficient for the calculation of the second and third moments of the degraded sample. When necessary, moments higher than the sixth were estimated roughly from the observed change in the first six moments. It was found that the ratio between one moment and the previous moment usually changed according to a linear function. The situation is illustrated by the series of moments shown as equation (31), where the successive ratios are 0.00151, 0.00181, 0.00204, 0.00218, and 0.00230. It was felt that values of the higher moments obtained by the extension of such a series were sufficiently accurate for the present purposes.

The operations involved are presented here in some detail for one case—namely, cotton cellulose

degraded in heterogeneous system; the particular degradation is that between one stage, *C*-4, degraded to another, *C*-6. The designation of stages here are those used in the work of Jörgensen [6]. For present purposes, the distribution at the earlier stage will be considered initial. For this stage, there were found the first six moments as follows:

$$\begin{aligned} \mu_1 &= 1160 & \mu_4 &= 6482\ (10)^9 \\ \mu_2 &= 1756\ (10)^3 & \mu_5 &= 1411\ (10)^{13} \\ \mu_3 &= 3181\ (10)^6 & \mu_6 &= 3240\ (10)^{16} \end{aligned} \qquad (31)$$

The degraded stage, *C*-6, arising from *C*-4 has the empirical moments:

$$\left.\begin{aligned} m_1 &= 980 \\ m_2 &= 1248\ (10)^3 \end{aligned}\right\} \qquad (32)$$

Accordingly, from equation (23):

$$\left.\begin{aligned} p &= (1160 - 980)/1160(981) = 0.00015818 \\ q &= 1 - p = 0.99984182 \end{aligned}\right\} \qquad (33)$$

From equations (33) and (31) the second moment expected (see equation (22)) for *C*-6 is

$$\begin{aligned} m_2 = 0.84495941(&1{,}159.8 + 1{,}755{,}444.5 \\ &- 167{,}681.1 + 13{,}510.1 - 930.6 + 56.3 \\ &- 3.1 + \ldots)^* = 1{,}353\ (10)^3 \end{aligned} \qquad (34)$$

The difference between the results of equation (34) and equation (32) is 8% of the former, which seems a very reasonable difference and is only of the magnitude of experimental error.

The above procedure was carried out for each of 22 other steps of degradation; at each step the situation at one stage was considered initial with respect to the situation at the next stage. The second moment of the later stage, as calculated from the moments of the preceding stage, is compared for each case in Table III with the observed second moment; the deviation of the latter from the former is also shown. A positive deviation means that the calculated value is higher than the found value. A positive deviation, accordingly, signifies that on the basis of random disjunction the second moment should have been higher than that actually found. A very close agreement between calculated and found values can hardly be expected for the reasons discussed in some detail below. A deviation of 10% may perhaps be regarded as permissible. The agreement between theory and observation in Table III should probably be considered good for all steps of degradation except those under heterogeneous conditions for spruce pulp.

It is of particular interest to compare with the results from the present theory the values of the second moment that would be obtained under what may be termed "Case II"—*i.e.*, the situation in which the initial material is assumed to be of uniform degree of polymerization. The problem may be illustrated by considering cotton at, say, stage *C*-6, with a mean value of $m_1 = 980$, when it is conceived as derived from a uniform starting material, *C*-4, with a mean of $\mu_1 = \lambda = 1160$. Employing these values p again takes the value shown in equation (33). Employing equation (29), the second moment of the degraded material should be $1070(10)^3$. This result is -17% in error from the found second moment. Parallel numerical analyses for all degradations are shown in Table III. It is obvious from this table that the assumption of Case II produces values for the second moment which are in greater deviation from the experimental values than are the results from the theory proposed in the present communication.

The treatment in connection with the second moment, m_2, as in Table III, is paralleled in Table IV for the third moment, m_3. In the heterogeneous degradation the spruce-pulp cellulose is not considered because the calculation of the second moments had already shown such great deviation that agreement in the third moment could be of no importance. Table IV shows the deviation of the theoretical, calculated third moment from that found experimentally. The effect of experimental error in the determination of the weight distributions will be greater for the third moment than for the second; this is so particularly for errors in the estimation of the amount of relatively highly polymerized material. Accordingly, deviations may permissibly be perhaps twice greater in Table IV than in Table III. The agreement of calculated third moments with found moments is reasonably good on the basis of the present theory, but very bad on the theory that arises from the assumption of uniform starting material.

The fact that the agreement of results and theory is almost as good for heterogeneous as for homogeneous degradation is worthy of some reflection. It might, erroneously, seem that since the heterogene-

* The last term shown in the series is found by taking $\mu_7 = 778\ (10)^{20}$.

TABLE III. SECOND MOMENTS AS CALCULATED AND FOUND UPON DEGRADATION

Material and degradation process	Second moment (divided by 10^8) of the later stage: Moment found	Theoretical moment	Theoretical deviation (%)	Calculated moment (Case II)*	Deviation (Case II) (%)
Homogeneous degradation					
Cotton					
CF–1 → *CF*–2	805.6	913.5	+12	769.6	−5
CF–2 → *CF*–3	398.1	432.7	+8	346.9	−15
CF–3 → *CF*–4	57.1	64.4	+11	59.0	+3
Spruce pulp					
SF–1 → *SF*–2	203.7	180.2	−13	115.0	−77
SF–2 → *SF*–3	81.5	83.2	+2	44.8	−82
SF–3 → *SF*–4	21.4	20.7	−3	12.1	−77
Aspen pulp					
AF–1 → *AF*–2	468.9	545.9	+14	460.3	−2
AF–2 → *AF*–3	227.8	293.4	+22	234.8	+3
AF–3 → *AF*–4	32.6	39.6	+18	37.3	+13
Heterogeneous degradation					
Cotton					
C–0 → *C*–1	5688.	5783.	+2	6077.	+6
C–1 → *C*–2	3526.	3999.	+12	3782.	+7
C–2 → *C*–4	1756.	1842.	+5	1752.	−0
C–4 → *C*–6	1248.	1353.	+8	1070.	−17
C–6 → *C*–8	564.8	632.6	+11	535.6	−5
C–8 → *C*–9	252.8	261.5	+3	220.5	−15
Spruce pulp					
SP–0 → *SP*–1	1021.7	975.2	−5	516.2	−98
SP–1 → *SP*–6	571.6	492.9	−16	240.3	−138
SP–6 → *SP*–7	317.7	227.2	−40	139.4	−128
SP–7 → *SP*–8	250.9	162.1	−55	71.2	−252
Aspen pulp					
A–*W* → *A*–0	2502.	2812.	+11	2642.	+5
A–0 → *A*–1	1832.	1940.	+6	1865.	+2
A–1 → *A*–7	1004.2	983.9	−2	815.6	−23
A–7 → *A*–9	599.3	644.8	+7	427.9	−40

* In Case II, it was assumed that the polymerization in the initial material was uniform.

ous cleavage is restricted mainly to the amorphous regions, it could not be random, with respect to position and size of molecule. In fact, the only difficulty arises if there exists a considerable probability of more than one break occurring in a given exposed part of a molecule—*i.e.*, a part involved in an amorphous region. Then there would be an interdependence of chances of breaking—*i.e.*, if one bond in a given position in a molecule is liable to breaking, some adjacent bonds are liable to breaking, whereas other bonds in the molecule are not so liable and the condition of independence of chances (necessary for randomness) is vitiated. If, however, the probability of cleavage within the amorphous regions is so small that more than one cleavage is unlikely, this difficulty becomes trivial. Since all parts of a molecule and molecules of all sizes are equally likely to be involved in an amorphous region, the equality of probability of any type of bond breaking is not affected. The departure from randomness should, accordingly, be slight as long as the chance of a bond in the amorphous regions breaking remains small—*i.e.*, when the general chance, p, as in equation (1), etc., of any bond breaking is small and a considerable part of the material occurs in amorphous regions. In the present illustrative material, as that of Tables III and IV, the conditions necessary for the

TABLE IV. THIRD MOMENTS AS CALCULATED AND FOUND UPON DEGRADATION

Material and degradation process	Third moment (divided by 10^6) of the later stage				
	Moment found	Theoretical moment	Theoretical deviation (%)	Calculated moment (Case II)*	Deviation (Case II) (%)
Homogeneous degradation					
Cotton					
CF-1 → *CF*-2	1108.	1421.	+22	855.	30
CF-2 → *CF*-3	415.4	483.3	+14	245.8	−69
CF-3 → *CF*-4	22.75	27.37	+17	22.96	+1
Spruce pulp					
SF-1 → *SF*-2	223.5	183.6	−22	50.6	−342
SF-2 → *SF*-3	47.48	50.98	+7	11.82	−302
SF-3 → *SF*-4	7.430	—†	—	1.875	−296
Aspen pulp					
AF-1 → *AF*-2	393.2	628.6	+37	381.0	−3
AF-2 → *AF*-3	131.2	218.9	+40	132.6	+1
AF-3 → *AF*-4	9.13	16.83	+46	11.80	+23
Heterogeneous degradation					
Cotton					
C-0 → *C*-1	15700.	16110.	+3	16800.	+7
C-1 → *C*-2	7730.	10450.	+26	8304.	+7
C-2 → *C*-4	3181.	3557.	+11	2875.	−11
C-4 → *C*-6	2033.	2328.	+13	1204.	−69
C-6 → *C*-8	686.0	853.5	+20	481.2	−43
C-8 → *C*-9	202.4	248.8	+19	129.2	−57
Aspen pulp					
A-*W* → *A*-0	4522.	5841.	+23	4920.	+8
A-0 → *A*-1	3013.	3386.	+11	2800.	−8
A-1 → *A*-7	1330.	1411.	+6	949.	−40
A-7 → *A*-9	719.7	709.9	−1	316.4	−127

* See footnote, Table III.
† Too slowly convergent to be calculated.

random cleavage under heterogeneous degradation were probably nearly satisfied for cotton and aspen cellulose but not satisfied for spruce pulp produced under the Mitscherlich process.

It will probably be granted that, in a general way, fairly good agreement has been found, on the basis of theory proposed in the present communication, between the calculated and empirical second and third moments, so that it should be regarded as quite probable that degradation is in large part a matter of the random disjunction of bonds. It is realized, however, that even if the present comparison were made on the basis of a very great number of moments and even if a very close correspondence were found, then, from a strictly mathematical viewpoint, random degradation would not be proven. There could possibly be found other theoretical models that could be justified in the same way as that here developed. Explicitly, the hypothetical model might be such that the relationship found between the moments of the partially degraded and initial distributions should obtain. It seems, however, very hard to conceive any such alternate theory on the basis of the generally accepted structural formula of the cellulose molecule.

A very close agreement cannot be expected in any operations such as those of Table III because there is considerable inaccuracy inherent in the experimental determination of the number distributions on which the moments in those operations were based. First of all, there is difficulty in the fractionation, particularly for the high-molecular part of the material. Secondly, there is some doubt whether the important straight-line relationship between degree of polymerization and intrinsic viscosity is valid when the degree of polymerization

exceeds a value of about 1500, as has been discussed by Jörgensen [6]. Thirdly, as has been discussed by Beall [1], there is considerable doubt as to whether the current numerical methods (used in the present study) for synthesis of the number distribution from the results of even very fine fractionation are correct.

It is hoped that current work with the ultracentrifuge, which can be used to obtain direct estimates of the statistical moments, will lead to further examination of the problem of random cleavage by the present methods. When the moments are more accurately determined, it is further hoped that the relationship between them will be determined so that the effects due to heterogeneous degradation will be involved and may be determined from the experimental evidence of the moments. It might, for instance, be possible to determine the average length of the crystalline regions from appropriate degree of degradation, in conjunction with appropriate accuracy of moments and using the proper statistical analysis.

Summary

There is developed a new treatment of the problem of the degradation of cellulose. This treatment restricts the study of the frequency distribution of cellulose of various degrees of polymerization to the calculation of statistical moments. By this restriction, great difficulties are avoided. It proved possible to consider a variety of cases without making any restriction as to the nature of the starting material. In general, the agreement between theoretical and actual results was good. This result substantiated the theory that the disjunction of the cellulose molecule, with hydrolytic cleavage, occurs randomly throughout the length of the molecule. The corresponding results, using existing theory which is based on a false assumption that the initial material is of uniform polymerization, gave very poor correspondence between theory and observation.

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The Plasticity of Wool*

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WHEN A LOAD is applied to wool fibers in water or saturated air at ordinary temperatures, immediate extension is followed by a slow creep, especially if the load is greater than the limit of the Hooke's Law region of the load-extension curve. In an early attempt [9] to discover the laws of creep, Cotswold wool fibers were allowed to extend under constant stress in saturated air, the load being applied in the form of a hyperbolic weight [1] which sank in water as extension took place in order to compensate for the diminishing cross-sectional area of the fiber. Under these conditions, using a stress of 6.89×10^5 g./cm.^{2} at 21°C, the extension, E, of one fiber increased from 19.4% after 3 min. to 30.2% after 300 min. and 68.4% after 18,682 min. [8]. There is an exponential approach to a limiting extension during the later stages of the process, a linear relationship being obtained when log $(70 - E)$ is plotted against time over the period from 1 to 13 days [10]. Since wool fibers may be stretched 25% without affecting the x-ray diagram [2, 3], deviations from the linear relationship seem to be associated with extension of the amorphous phase of the fiber, and the relationship itself is thought to express the rate of unfolding of the molecules of α-keratin in the crystalline phase. Using the data for the rate of extension of wool fibers in saturated air at 13°C and 21°C under different stresses, a preliminary estimate of 20 kg.-cal. for the activation energy of the unfolding process was obtained [10], but the nature of the rate-determining reaction, whether hydrogen-bond breakdown or disulfide-bond hydrolysis, is unknown. The primary object of the present investigation was to identify the reaction.

Experimental Procedure and Results

The experiments discussed above were carried out about 25 years ago, before the main features of the molecular structure of wool had been elucidated. It now seems clear that the use of hyperbolic weights to compensate for the diminishing cross-sectional area of the fiber during extension was both unnecessary and incorrect. Since wool fibers return exactly to their original length on being released in water, even from extensions as high as 70%, extension must proceed by molecular unfolding without slip, and the load is carried by the same number of chain molecules throughout the process. Data of greater theoretical significance should therefore be obtained by studying the extension of wool fibers under constant load, and this procedure has been adopted in the present investigation.

Most of the experiments were carried out with fibers taken from one lock of Lincoln wool, which was selected for use because the variation in diameter along the length of the fibers was small. After the wool had been purified by extraction with alcohol and ether in a Soxhlet apparatus, followed by washing in distilled water, it was pressed between filter papers and allowed to dry in room air. Except for special purposes, only the root ends of nonmedullated fibers were used, each 5-cm. length being attached to light glass hooks with a solution of polymethyl methacrylate in chloroform, as shown in Figure 1. In order to avoid errors due to possible creep of the fiber through the cement under prolonged application of stress, tiny drops of the solution were touched to the fiber near each hook to serve as reference points for the precise measurement of length. When the cement was dry, the diameter of the fiber was measured at 50 places along its length by means of a microscope fitted with a calibrated eyepiece micrometer. The cross-sectional area and the load needed to give the required stress were then calculated.

At this stage the fiber was sometimes calibrated by determining its load-extension curve up to 30% extension in distilled water at 22.2°C by means of the Cambridge Fibre Extensometer. During such an

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extension the fiber suffers little or no permanent alteration in properties [8], provided extension is carried out rapidly, and the work required for 30% extension was derived from the area between the load-extension curve and the axis of extension. The purpose of calibrating the fiber in this way was to discover whether there is any relationship between the work required for 30% extension and the rate of creep under constant load.

After a 24-hr. rest in distilled water, the calibrated fiber was transferred to a vertical tube containing distilled water. The lower hook was engaged with the hook sealed into the tube, while the fine silk thread attached to the upper hook was carried over a frictionless pulley, as shown in Figure 1. The fiber was then drawn taut; after its unstretched length had been measured, a glass tube, adjusted to the desired weight with copper turnings, was engaged with the free hook of the silk thread and lowered gradually to apply the stress. Temperature control was maintained with a water thermostat, and the extension of the fiber was determined at intervals with a travelling microscope until the fiber broke. Typical data for a fiber which was allowed to extend under a load of 7×10^5 g./cm.^{2} at 22.2°C are given in Table I and illustrated (in part) by curve 1 of Figure 2.

There is an exponential approach to a limiting extension of 75% during the later stages of extension, and the linear relationship between log $(75 - E)$ and t over the period from 2,000 to 10,000 min. is illustrated by curve 1 of Figure 3. Once it had thus been shown that a simple law of creep could be obtained by studying the extension of fibers under constant load instead of, as formerly, under constant stress, data were obtained for a large number of fibers under a load of 7×10^5 g./cm.^{2} at 22.2°C. An exponential approach to a limiting extension was

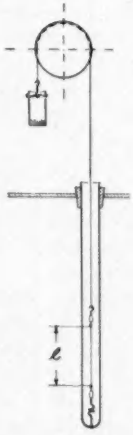

FIG. 1. *Schematic diagram of apparatus used to study extension of single fibers in water under constant load.*

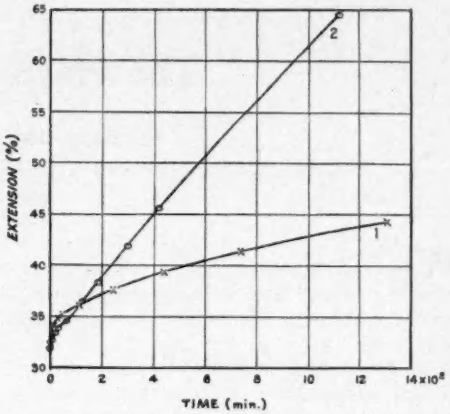

FIG. 2. *Extension of single wool fibers in water under constant load as a function of time.* Curve 1—*Fiber exhibiting normal rate of relaxation.* Curve 2—*Fiber showing abnormally high rate of relaxation.*

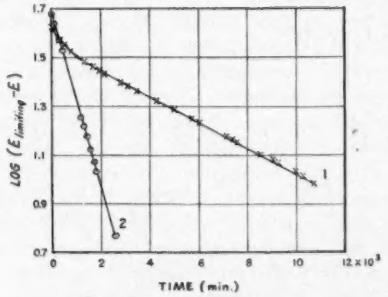

FIG. 3. *Extension of single wool fibers in water under constant load as a function of time. The original data are the same as in Figure 2, but here the common logarithm of the difference between the limiting extension,* $E_{limiting}$, *and the extension,* E, *is plotted against time. For fiber 1 (normal relaxation) of Figure 1, the limiting extension is 75%. For fiber 2 (abnormally high relaxation) of Figure 1, the limiting extension is 79%.*

TABLE I. Fiber Diameter, 53.3μ; Coefficient of Variation of Diameter, 5.4%

Time (min.)	Extension (%)
1	32.1
3	33.0
5	33.4
8	33.7
16	34.2
32	34.8
50	35.2
110	36.1
240	37.7
440	39.4
740	41.3
1,310	44.2
1,460	44.9
1,630	45.8
1,900	46.9
2,090	47.8
2,760	49.9
2,950	50.5
3,080	50.9
3,460	51.9
4,280	54.0
4,970	55.6
5,720	57.2
6,000	57.9
6,320	58.6
7,120	60.0
7,360	60.4
7,540	60.7
8,520	62.3
9,020	62.9
9,230	63.3
9,950	64.3
10,260	64.7
10,680	65.4

observed in all cases, but the limiting extension, usually 75%, varied from 75% to 85%. The slopes, k, of the lines obtained by plotting log $(75 - E)$ against time (min.) for the main group of fibers are given in Table II, which includes values for the work required to stretch the fibers 30% during the preliminary calibration.

Before discussing the results, attention must be drawn to the fact that the fibers, being only roughly circular in cross section, are more uniform in cross-sectional area than is indicated by the values given in Table II for the coefficient of variation in diameter. There need be no surprise, therefore, that the values for the extension after 1 min.; the slope, k; and the work per unit volume for 30% extension show no connection with the variation in diameter.

The most interesting feature of the results is, of course, the far greater variation in k than in the work per unit volume for 30% extension; referred to the lowest value in each case, the variation in k

TABLE II

Diameter (μ)	Coefficient of variation (%)	Extension after 1 min. (%)	Slope k (min.$^{-1}$)	Work/volume* (g.-cm./cm.^{3})
41.2	5.9	31.8	-3.83×10^{-6}	1.48×10^{-6}
42.6	5.1	32.3	−4.91	1.48
51.4	8.8	31.8	−5.00	1.44
53.3	5.4	32.1	−5.12	1.46
49.6	7.7	31.9	−5.46	1.49
42.3	8.2	33.1	−5.52	1.40
54.1	6.9	31.5	−5.69	1.53
47.1	6.3	32.5	−5.78	1.47
53.4	5.5	32.6	−5.86	1.43
47.6	10.2	33.5	−5.96	1.38
49.4	6.0	31.3	−6.17	1.52
41.2	6.6	32.2	−6.32	1.44
50.1	7.6	32.9	−6.34	1.45
53.8	6.9	34.1	−6.43	1.33
41.9	5.7	32.2	−6.53	1.51
47.8	5.2	32.2	−6.57	1.49
44.1	10.7	31.1	−7.63	1.54
52.8	7.0	32.7	−7.77	1.47
43.7	8.5	32.7	−8.21	1.45
43.8	5.9	31.7	−8.29	1.52
51.8	10.6	34.3	−8.72	1.33
49.4	10.0	33.3	−8.98	1.40
45.9	8.6	33.5	−10.6	1.43

* Work required to stretch the fibers 30%.

is 177%, compared with 15.8% for the work. Differences between fibers are thus more readily revealed by plasticity measurements, which are especially important because of the part played by creep and relaxation in the processes of the wool textile industry. Such measurements may indeed provide a simple numerical expression, in values of k, for describing the differences between wools which have so far eluded the scientist but which the craftsman recognizes by combining visual and tactile judgment with impressions formed during years of experience in processing various types of wool.

The variation in k is, however, much greater than has so far been indicated. The full extent of its variation is shown in Table III, where the values for the 75 fibers examined in this and subsequent experiments under a stress of 7×10^5 g./cm.^{2} are summarized.

In the light of these results it seemed desirable, before proceeding further with the investigation, to discover whether the variability of Lincoln wool is exceptional. Similar experiments were therefore carried out with human hair, which has the special advantage of fibers being far more uniform in cross-sectional area than wool fibers. The results obtained

TABLE III

Range in $-k$ (min.$^{-1}$)	Number of fibers
$3–5 \times 10^{-5}$	4
5–7	35
7–9	16
9–11	8
11–13	4
13–15	2
15–17	—
17–19	1
>35	5

TABLE IV

Cross-sectional area (μ^2)	Limiting extension (%)	Extension after 1 min. (%)	Slope k (min.$^{-1}$)
2621	84	25.7	-5.18×10^{-5}
2510	86	25.5	−9.76
2494	88	25.5	−10.04
3475	86	24.8	−10.56
3738	87	25.0	−10.64
2975	86	24.6	−10.72
3981	86	24.4	−11.29
3161	86	24.9	−12.03
3416	90	24.2	−43.40

with fibers which were allowed to extend in water at 25°C under a load of 6×10^5 g./cm.^{2} are given in Table IV.

There can be no doubt, therefore, that the variability of k is not peculiar to Lincoln wool, nor is it due to variations in cross-sectional area of the fibers along their length. In consequence, attention was again turned to Lincoln wool and the group of five fibers with abnormally high values of k (last entry in Table III). Full details of their behavior are given in Table V; the linear relationship between log $(79 - E)$ and time for the third of the fibers is illustrated by curve 2 of Figure 3.

A curious difference between fibers with high and low values of k is revealed, however, when their extension-time curves are compared. Curve 2 of Figure 2 is typical of fibers giving the highest values of k. In the early stages of extension, up to 60 min., it has the same form as curve 1 for the fiber with a k value of -5.12×10^{-5} min.$^{-1}$, but there is then a sharp upward turn which is associated with the high value of k. It seems clear that some primary resistance must be broken down before rapid extension can take place, and since the cuticle of human hair fibers is known to be less extensible than the cortex, wool fibers which had undergone slow extension in water at 22.2°C were examined under the microscope to discover whether the cuticle was broken. Even after staining with methylene blue, however, no such fissures as are observed in the cuticle of human hair fibers at extensions of 45% to 50% could be detected in wool fibers which had been stretched 70%. In the light of these observations, it seemed probable that the explanation of the shape of curve 2 of Figure 2 was to be found in the fine structure of the fibers.

Although the amorphous and crystalline regions of the wool fiber are in series and in parallel with one another, the amorphous phase is the first to extend when a load is applied because the folded chain molecules are not normally cross-linked in three dimensions. In the idealized structure, with cross-linking in one plane to form grids of folded molecules, extension of the amorphous region of one grid is not likely to be seriously restricted by the proximity, in a neighboring grid, of a less easily extended crystalline region. But the structure of the wool fiber departs from this ideal. The disorganization of the amorphous phase is due, in part at least, to the wandering of the chain molecules from one grid to another, thus giving the effect of three-dimensional cross-linking in the amorphous phase. The very conditions which give rise to imperfections in the fine structure of the wool fiber create the three-dimensional cross-linking which causes the amorphous and crystalline regions to interfere seriously with one another during extension. Just as in the idealized structure, the amorphous region is the first

TABLE V

Diameter (μ)	Coefficient of variation (%)	Limiting extension (%)	Extension after 1 min. (%)	Slope k (min.$^{-1}$)	Work/volume (g.-cm./cm.^{3})
50.5	5.1	80	35.3	-48.6×10^{-5}	1.53×10^{-6}
47.6	6.6	80	31.8	−37.6	1.55
46.4	5.6	79	31.3	−35.3	1.57
49.4	7.8	80	31.7	−50.2	1.54
47.9	7.5	80	32.6	−50.2	1.49

TABLE VI

Group No.	Total number of fibers	Number of fibers of known k	Average value of k (min.$^{-1}$)	Sulfur content (%)	Sulfur content × k
1	18	13	-24.7×10^{-4}	0.98	-24.2×10^{-4}
2	15	12	−8.71	2.27	−19.8
3	30	30	−5.97	3.97	−23.7

to extend under load, but the extension realized depends upon the amount of three-dimensional cross-linking; and the rate of creep, due to subsequent unfolding of the chain molecules in the crystalline phase, is governed to a large extent by breakdown of cross-linkages, especially those which give the effect of three-dimensional cross-linking. In terms of this hypothesis, the rapid upward turn of curve 2 of Figure 2 at 35% extension would, then, be due to disulfide-bond breakdown. Its effect in promoting rapid extension will, of course, be especially pronounced when the number of cross-linkages—*i.e.*, the sulfur content of the fibers—is small, and the fibers of curves 1 and 2 should, therefore, differ in having high and low sulfur contents, respectively. More generally, there should be an inverse relationship between the sulfur contents of the fibers and their k values.

In order to test the hypothesis, all the fibers examined (63 at this stage of the investigation) were classified into three groups, according to their rates of extension in distilled water at 22.2°C under a load of 7×10^5 g./cm.^{2}, for determinations of sulfur content. Sufficient material for analysis was obtained by including in each group of fibers those which broke at too low an extension to give reliable values of k. In such cases, classification was based on similarities of extension-time curves with those of fibers with known values of k. The results are given in Table VI.

In agreement with the above hypothesis, there is an inverse relationship between the k values of the fibers and their sulfur contents. Although the latter were determined on samples weighing only 1.2–2.4 mg., and although the exact value of k appropriate to the sulfur content is known only for group 3, the product of k and sulfur content (Table VI) is remarkably constant. Further support for this relationship is provided by the following considerations. If there were no cystine cross-linkages between the polypeptide chains, the rate of extension under the usual conditions would be extremely high; if the number of cross-linkages were the greatest possible, the rate of creep would be infinitely slow. Should it be confirmed with other types of wool, the hyperbolic relationship between k and sulfur content will provide a simple means of estimating the sulfur content of single fibers. It will allow fibers to be classified for use in studying relationships between sulfur content and molecular structure, swelling in various media, and rate of uptake of dyes, as well as in the work which is now being undertaken to discover the origin of the remarkable variations in the sulfur content of fibers within a single lock of wool.

Further support for the view that the rate of creep of wool fibers is governed by their sulfur content was obtained by comparing the rates of extension of root and middle sections of the same fibers. The sulfur content of wool fibers is known to vary along their length, in accordance with variations in the nutritional value of the pasture throughout the year [4], and there should be corresponding variations in rate of creep. Observations were confined to root and middle sections of the fibers in order to avoid complications due to the action of light and air on the tip section during growth [7]. In all cases, the rate of creep of the root section was found to be less than that of the middle section, and typical values of k for fibers which were allowed to extend in water at 32.2°C under a load of 5×10^5 g./cm.^{2} are given in Table VII.

TABLE VII

Fiber No.	Section	Diameter (μ)	Coefficient of variation (%)	Limiting extension (%)	Slope k (min.$^{-1}$)
1	Root	40.0	5.8	65	-8.7×10^{-4}
	Middle	50.2	8.9	70	−10.4
2	Root	42.9	6.0	67	−6.9
	Middle	57.6	6.3	70	−15.6
3	Root	41.0	6.0	70	−3.3
	Middle	56.1	6.0	68	−8.8

Unfortunately, because the remaining fibers in the tuft of Lincoln wool were required for other purposes, it was impossible to determine the sulfur contents of the root and middle sections of the staple, but the results given are satisfactory in being consistent with the general hypothesis that the rate of creep of wool fibers is governed by their sulfur content.

Further evidence in support of this view was obtained by comparing the rates of creep of human hair fibers in water and in 0.1*N* hydrochloric acid at 22.2°C. Typical extension-time curves are shown in Figure 4; in conformity with the greater stability of the cystine disulfide bond in acid solution, the rate of creep and ultimate extension of the fibers are far higher in water than in 0.1*N* hydrochloric acid under the same load.

In addition, the creep of fibers which had been treated with potassium cyanide to convert cystine disulfide bonds into the more stable lanthionine cross-linkages [5] was examined. A few fibers of human hair were treated with 1% potassium cyanide solution for 16 hrs. at 65°C, washed in running water overnight, and then allowed to extend in distilled water at 22.2°C under a load of 4×10^5 g./cm.^{2}. The immediate extension of the fibers was greater than that of untreated fibers, owing to the damage they sustained during treatment, but the rate of creep was so slow that the extension-time curves were intersected by those for untreated fibers. Considerable support is thus given to the view that the rate of creep of animal fibers in water is governed, to a large extent, by disulfide-bond breakdown.

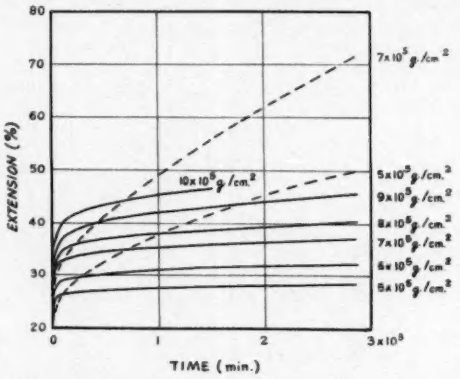

FIG. 4. *Extension of human hair fiber under constant load as a function of time: in water (broken lines); and in 0.1N hydrochloric acid (solid lines).*

TABLE VIII

Temperature (°C)	Stress (g./cm.²)	Number of fibers examined	Extension after 1 min.	Slope k (min.$^{-1}$)
22.2	5×10^5	19	18.8	-2.61×10^{-5}
	6	19	28.2	−4.97
	7	75	32.4	−9.96
	8	18	33.5	−17.13
32.2	5	19	22.0	−10.25
	6	19	29.9	−25.23
	7	14	32.8	−39.32
	8	13	35.4	−73.96

If, as has so far been argued, creep is governed by disulfide-bond breakdown (hydrolysis), the activation energy of the process should be high. Accordingly, the rates of creep of wool fibers under various stresses at 22.2°C and 32.2°C were determined. Most of the fibers had not been subjected to previous extension; the results are given in Table VIII.

As will be shown in a later paper, there is theoretical justification for the linear relationship between log k and stress, which is illustrated in Figure 5.

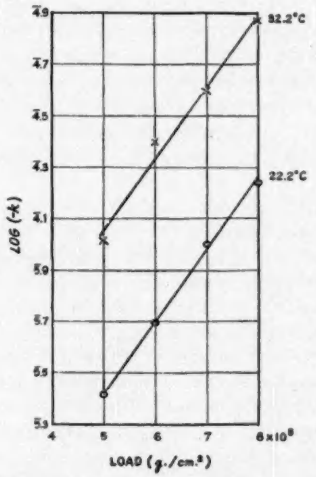

FIG. 5. *Relationships between the common logarithm of −k and load at 22.2°C and 32.2°C.*

TABLE IX

Stress (g./cm.²)	ΔH^* (kg.-cal.)
5×10^8	24.4
6	29.0
7	24.5
8	26.1

The activation energies were calculated from corresponding values of k by means of the equation

$$\Delta H^* = \frac{RT_1T_2\Delta \ln k}{T_2 - T_1},$$

and the results are given in Table IX.

Taking into account the variability of k, the results obtained at different stresses are in fair agreement, and the average value of ΔH^* (26 kg.-cal.) is not inconsistent with the theory of disulfide-bond hydrolysis because Eyring and Stearn [6] have shown that the value of ΔH for the hydrolysis of cystine with dilute hydrochloric acid is approximately 20 kg.-cal.

Summary

When wool fibers are allowed to extend under constant load in distilled water at ordinary temperatures, there is an exponential approach of the extension, E, to a limiting extension, $E_{limiting}$. The slopes, k, of the lines obtained by plotting log $(E_{limiting} - E)$ against t indicate the rate of unfolding of the molecules in the crystalline phase. Under the same load the value of k was found to be decidedly variable, even with fibers taken from a single lock of Lincoln wool; and determinations of sulfur content, after the fibers had been classified into three groups according to their rates of extension, showed that k varies inversely with the sulfur content.

Disulfide-bond breakdown appears to be essential to creep because the migration of chain molecules from one grid to another in the amorphous phase gives the effect of three-dimensional cross-linking and causes mutual interference, during extension, of the amorphous and crystalline phases, which are arranged in series and in parallel with one another. In agreement with this deduction, and with the known variation in sulfur content along the length of wool fibers, different values of k were obtained for the root and middle sections of the same fibers. Further, far higher values of k were obtained with normal fibers than with others which had been treated with potassium cyanide in order to convert cystine into lanthionine cross-linkages, which are more stable; and the rate of creep of untreated fibers in hydrochloric acid at pH 1 is less than in water under the same conditions of temperature and stress owing to the greater stability of the cystine cross-linkages at low pH values.

Using a series of stresses, k has been determined for Lincoln wool at 22.2°C and 32.2°C. There is a linear relationship between log k and stress for each temperature, and the activation energy, ΔH^*, of creep as a first-order reaction is about 26 kg.-cal., which is consistent with the value of ΔH (20 kg.-cal.) for the hydrolysis of cystine with dilute hydrochloric acid.

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The Chemical Modification of Wool—Treatment with Formaldehyde Solutions

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Abstract

A study was made of the reaction of formaldehyde with wool in order to determine optimal conditions for the production of wool that is more stable to alkali, as measured by the alkali-solubility test. Extremely mild treatments with dilute formaldehyde solutions confer an appreciable degree of alkali-resistance to the wool, presumably by the formation of cross-links, and optimal alkali-resistance was obtained by treatment with 0.5% formaldehyde solutions at pH 6 to 8 for 6 hrs. at 50°C. Under these conditions, cystine linkages are not involved to any appreciable extent, and the acid-combining capacity of the wool is changed only slightly. Although loss of sulfur from formaldehyde-treated wool occurs readily on treatment with hot alkaline solutions, the rate of loss of both sulfur and weight is less than in the case of untreated wool. The chemical evidence cited is in agreement with the view expressed elsewhere that additional cross-linkages are introduced in the wool molecule as a result of treatment with formaldehyde solutions. The lability of these new cross-linkages on exposure to acidic or hydrolytic conditions is noted, and this behavior is compared with that of wool modified by other chemical reactions. Some comparisons are made with the use of the formaldehyde reaction in the regenerated protein-fiber field.

Introduction

Long before very much was known about wool structure and the role of disulfide bonds in it, attempts were made to render wool stable to alkaline media because of the damage caused by exposure to alkali in normal textile processing. The reaction of wool with formaldehyde was advanced as a method for the protection of wool from alkaline degradation almost a half century ago [10]. The reaction of wool with formaldehyde has also been proposed as a means of preventing damage from excessive boiling in water, from exposure to alkaline solutions of reducing agents, from dyeing operations, and from moth and bacterial attack [27]. Interestingly enough, the preparation of regenerated protein fibers, involving treatment of the filaments with formaldehyde solutions, was also advanced about 50 years ago [26]. The use of the formaldehyde reaction in tanning leather has also been known for many years. Obviously, in both cases the function is to "insolubilize" the parent protein so that it is stable to various aqueous media which would otherwise produce undesirable effects. In the case of regenerated protein fibers, which in recent years have achieved commercial production both here and abroad, the formaldehyde reaction has received extensive investigation, especially since Lanital was introduced commercially in Italy 15 years ago [1]. Despite the fact that this reaction is complicated and leaves much to be desired, it is still an integral step which is used in the preparation of all commercially acceptable regenerated protein fibers. On the other hand, the treatment of wool with formaldehyde has achieved little or no commercial importance.

The main purpose of this work was the investigation of the optimal reaction conditions for the production of wool which is resistant to alkalies. Although many investigations on this reaction have been reported, no comprehensive study of the alkali-resistance conferred on the wool has been found. Using the alkali-solubility test, which is now widely used in the textile industry for the measurement of alkali-resistance, the effects of various conditions in the formaldehyde reaction with wool have been studied. This analytical tool is of particular interest in such a study because alkali-solubility is greatly in-

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fluenced by the over-all molecular structure, and, as the molecular network is disturbed by rupture of disulfide groups so that smaller effective chain fragments may be formed, alkali-solubility increases. Conversely, as additional cross-links are introduced, or as chemically stable cross-links replace disulfide groups, alkali-solubility values decrease. Thus, information on the mechanism of the reaction was also obtained. For example, at ordinary temperatures the reaction of formaldehyde with wool does not involve modification of disulfide bonds [16], and, therefore, it is of particular interest because it provides for the possibility of introducing new cross-linkages into the keratin molecule in addition to those due to cystine.

Numerous references to the reaction of wool with formaldehyde were included in recent general review articles [6, 27]. The early investigations mentioned therein established the fact that formaldehyde reacted with the free amino group of the lysine side-chain over a wide range of pH up to approximately pH 8. At higher pH, the arginine side-chain also reacted with formaldehyde. More recently, Middlebrook and Phillips showed that formaldehyde did not react with the disulfide bond in wool at room temperature, but did at elevated temperatures [16, 17]. Fraenkel-Conrat [2] has shown that amide groups in wool also react with formaldehyde, and he further defined the conditions for reaction with arginine side-chains [4]. Middlebrook [15] reported similar observations, and also showed that some of the formaldehyde that combined with wool could not be removed by acid hydrolysis. Steinhardt [21] described the effects of formaldehyde on the titration curves of wool, and also indicated the participation of lysine and arginine side-chains in the reaction. Stoves [22, 23, 24] defined optimal conditions for the reaction based on improved mechanical properties, and found that optimal properties were produced by boiling with a 2% formaldehyde solution for 1 hr. at pH 7. Speakman and Peill [20], using the 30% index as a criterion of reaction, also reported optimal reaction conditions for formation of cross-linkages.

Materials and Methods

Both 4-ply worsted yarns and raw stock were used in this investigation. The yarns were extracted with Stoddard solvent, ether, and alcohol, and were then washed with water. The wool fibers (56–60's) were part of a lot used in previous investigations [7] and had been subjected to no mechanical or chemical treatment other than successive extractions with alcohol and ether for 5 hrs. each, followed by washing with water at 40°C.

In studying the reaction variables, the yarn was placed in the flask after the solutions were heated to the desired temperature in a constant-temperature bath. Commercial formalin was used in all cases. On completion of the reaction, the samples were thoroughly rinsed in water and allowed to dry at room temperature.

Cystine was determined by the method of Sullivan [25], as previously described [9]. Tyrosine was determined by Lugg's method [12] after hydrolysis with 6*N* NaOH for 20 hrs. at 105°C. Sulfur determinations were made by the oxygen-bomb method [14]. Alkali solubility was measured by the method of Harris and Smith [8]. The method involves treatment of the wool sample with 0.1*N* NaOH for 1 hr. at 65°C; the weight loss (%) represents the alkali solubility of the sample.

Results and Discussion

Effects of Variables

The effect on the alkali solubility of varying the concentration of formaldehyde in solution is shown in Table I. Protection against the action of alkali is given by exceedingly low concentrations of formaldehyde, and the optimal effect is obtained with 0.5% solutions.

The effect of the temperature of the reaction mixture on the alkali solubility is shown in Table II. Optimal protection is attained at a temperature of 50°C and higher, although marked protection is obtained by treatment at 25°C.

TABLE I. Effect of Concentration of Formaldehyde in Solution on the Alkali Solubility of Treated Wool *

Concentration of formaldehyde (%)	Alkali solubility (%)
0.0	11.6
0.1	3.9
0.3	3.3
0.5	2.8
1.0	2.9
5.0	3.4
10.0	3.9

* Treatment was at pH 8, 50°C, for 24 hrs.

TABLE II. EFFECT OF TEMPERATURE OF THE TREATMENT * ON THE ALKALI SOLUBILITY OF TREATED WOOL

Temperature (°C)	Alkali solubility (%)
Untreated	12.0
25	3.7
50	2.7
65	2.7
80	3.1

* Wool was treated with 1% formaldehyde solution at pH 6 for 24 hrs.

The effect of the duration of treatment on the alkali solubility is shown in Table III. Although considerable protection is produced in 30 min., the optimal effect was noted after 6 hrs. of reaction.

Alkali-solubility values for wool yarn which was treated for 6 hrs. at 50°C in buffered solutions containing 1% formaldehyde are given in Table IV. Since treatment in aqueous solutions alone, especially at high pH, affects alkali-solubility values due to lanthionine formation from disulfide linkages [11], values for samples treated in the buffer solutions alone are also given. These data show that alkali protection is afforded by formaldehyde treatment over the entire pH range, with optimal protection being produced by treatments in the range of pH 6 to 8.

Influence on Acid-Binding Capacity

The values for the acid-binding capacity of the treated yarns were determined, the data being shown in Table IV. A slight decrease, 0.1 meq./g., was noted in samples treated on the alkaline side, indicating the participation of some basic groups under these conditions. Since the primary amino groups of lysine can be converted to methylol groups, or secondary amino groups, which would still bind one equivalent of acid per original amino group, this slight decrease in acid-binding capacity is not unexpected.

Effect of Prolonged Alkaline Action

The stability of the modified wool samples to prolonged treatment under the conditions of the alkali-solubility test was determined by measuring loss in weight as a function of time. At the same time, loss of sulfur was measured to discover whether the cystine linkage itself had been stabilized. The results are shown in Figures 1 and 2.

TABLE III. EFFECT OF THE DURATION OF TREATMENT * ON THE ALKALI SOLUBILITY OF TREATED WOOL

Time (hrs.)	Alkali solubility (%)
Untreated	12.0
0.5	5.3
1.0	4.4
2.0	3.6
6.0	3.3
16.0	3.2
24.0	3.0
48.0	3.0

* Wool was treated with 1% formaldehyde solution at pH 6 at 50°C.

TABLE IV. EFFECT OF pH OF THE FORMALDEHYDE SOLUTION ON THE ALKALI SOLUBILITY OF TREATED WOOL

pH	Alkali solubility Control* (%)	Alkali solubility Treated† (%)	Acid-binding capacity (meq./g.)
Untreated	12.0	—	0.78
1	14.9	5.4	0.74
2	17.4	5.5	0.74
4	15.4	4.6	—
6	13.2	3.3	0.71
8	11.5	3.0	0.69
10	8.6	3.8	0.68

* Wool treated in solutions of indicated pH for 6 hrs. at 50°C.

† Wool treated in 1% formaldehyde solutions of indicated pH for 6 hrs. at 50°C.

The untreated wool shows progressive weight loss under these conditions so that in 8 hrs. 58.5% of the wool had dissolved. The formaldehyde-treated wool also shows progressive weight loss but at a much slower rate, especially in the first 7 hrs. of treatment. After 8 hrs., only 24% of the treated wool had dissolved. The curve for loss in weight of wool stabilized by reduction with thioglycolate and subsequent alkylation with 1,3-dibromopropane [18] is also included. This curve demonstrates that chemical modification of cystine linkages to convert them to an equal number of *bis*-thioether linkages effectively promotes alkali-resistance of the same degree as that conferred by formaldehyde treatment. On treatment of the reduced and alkylated wool with formaldehyde, additional protection to alkaline action is obtained; this result is also shown in Figure 1. Again, evidence for additional cross-linkages produced by the formaldehyde treatment other than those involving modification of disulfide bonds is indicated.

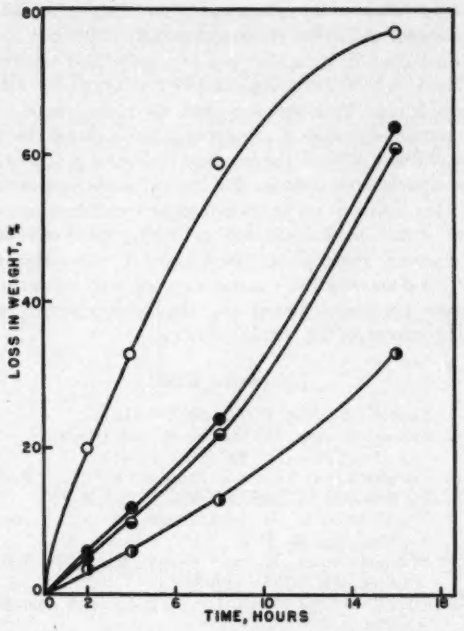

FIG. 1. *The loss in weight of wool samples during treatment with* 0.1N *NaOH at 65°C.* ○—*Untreated.* ●—*HCHO-treated.* ◒—*Reduced with thioglycolate and alkylated with 1,3-dibromopropane* [18]. ◑—*Reduced with thioglycolate and alkylated with 1,3-dibromopropane, and then treated with 1% formaldehyde, pH 6, for 6 hrs. at 50°C.*

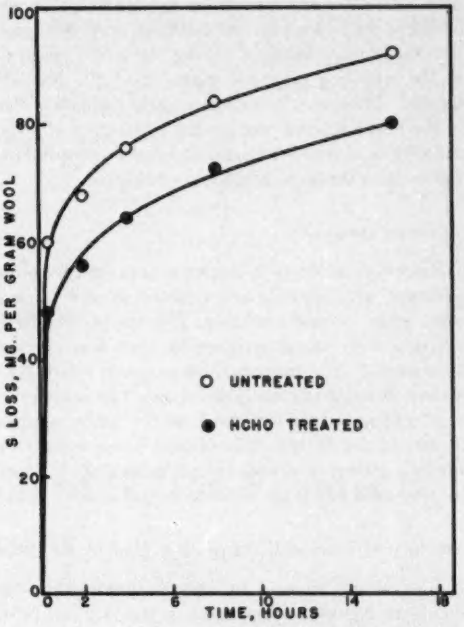

FIG. 2. *The loss in sulfur, as inorganic sulfide, from untreated and formaldehyde-treated wools during treatment with* 0.1N *NaOH at 65°C.*

The data for loss in sulfur are plotted in Figure 2. At all times, the total loss of sulfur was slightly greater from the untreated wool than from the modified wool. Under these conditions, half the total sulfur is removed from the untreated wool in less than 1 hr., and from the treated wool in 2.5 hrs. This result is of interest in view of recent work on the modification of keratin in which it was noted that cystine reactivity is apparently influenced by modification of the polar groups of adjacent amino acid side-chains in wool by methylation [19] or by treatment with propiolactone [13]. Another interesting observation can be made by comparing loss in sulfur with weight loss during the alkaline treatment. The ratios show that more untreated than treated wool is dissolved when a given loss in sulfur content is attained, especially during the first 2 hrs. of reaction. Such a stabilizing effect would be expected if additional cross-links were introduced into the wool molecule by the formaldehyde reaction, as has been demonstrated for other proteins [3].

Cystine Analyses

A number of the treated wools listed in Tables I and II were analyzed for cystine. The untreated wool had a cystine content of 12.3%, and the wool samples treated with solutions containing up to 1% formaldehyde had cystine contents of approximately 11%. Even when the formaldehyde in solution was increased to 10%, the cystine content dropped only to 9.4%. Thus, under these mild conditions, little disulfide sulfur participated, as previously noted by others [16]. Since formaldehyde interferes somewhat in the Sullivan method for the determination of cystine, it is likely that even less cystine than indicated was modified—for example, when formaldehyde equivalent to the amount which could com-

bine with all of the free amino groups of lysine was added to the hydrolyzate of untreated wool (to simulate the amount released during the acid hydrolysis of the wool), a cystine content of 11.5% was obtained. These cystine analyses again emphasize that in the formaldehyde reaction the production of alkali stability is obtained through additional cross-linking rather than through disulfide modification.

Tyrosine Analyses

Since formaldehyde is known to form condensation products with phenols and tyrosine groups in proteins under certain conditions [5], the possibility of reaction with bound tyrosine in wool was checked by analysis. The treated wools prepared by the conditions described in the tables showed the same tyrosine content as the untreated wool. Since tyrosine is determined in the hydrolyzates, these results do not rule against reversibly bound formaldehyde which may be split off in the alkaline hydrolysis.

Stability of Treated Wool to Acid Hydrolysis

The lability to acid hydrolysis of formaldehyde bound to regenerated proteins is well known [15], as is the loss of enhanced mechanical properties of formaldehyde-treated wool after acid boiling [24]. Experiments showed that after boiling the treated wool with 0.1*N* hydrochloric acid the resistance to alkali was lost. Thus, wool treated with formaldehyde so that it had an alkali solubility of 2.3% after the treatment had an alkali-solubility value equal to that of the untreated wool after the treated wool was boiled in 0.1*N* acid for 1 hr. This behavior demonstrates the main difference between formaldehyde-treated wool and wool stabilized by reduction and alkylation with alkylene dihalides. Both modification reactions produce wool which is resistant to alkaline action. However, whereas the alkali stability of the formaldehyde-treated wool is lost after boiling with acidic liquors, such as those used in dye baths, the alkali stability of the reduced and alkylated wools is unaffected by such acidic treatments. This is the great disadvantage of simple formaldehyde treatment. From an over-all simplified viewpoint, treatment with formaldehyde does to wool, in a qualitative manner, essentially what it does to synthetic protein fibers—that is, it introduces additional cross-linkages. However, since wool has so many disulfide cross-linkages in its structure originally, the beneficial effect of the additional cross-linkages on mechanical properties is, quantitatively, much less for wool than it is in the case of regenerated protein fibers, where the cross-linkages introduced by formaldehyde treatment are vital for maintenance of desirable mechanical properties. Since, in addition, in the case of wool, the enhanced resistance to alkaline treatments imparted by the formaldehyde treatment is not stable to acidic or hydrolytic treatments, such as would be encountered in dyeing processes or steaming, these points taken together may indicate the reason why the reaction of wool with formaldehyde has not achieved any significant commercial importance in the textile industry.

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Extension and Relaxation of Nylon Filaments

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Abstract

Measurements were made of the extension of nylon filaments under conditions of constant load for various lengths of time in air at 65% R.H. and in water. The extent of the recovery which took place after removal of the load was observed, and its dependence upon the magnitude and time of application of load, as well as upon the immersion medium, was determined. Further recovery which could be effected by treatment with heat or swelling agents was investigated. Limitations in the use of the terms "elastic limit" and "nonrecoverable deformation" when applied to textile fibers are pointed out.

THE EXTENT to which a fiber recovers from deformation and the factors which influence that recovery are important considerations from both a practical and a theoretical viewpoint. The practical aspect is exemplified in various ways in mill operation and in the finished fabric, the relaxation shrinkage of which is perhaps the most obvious effect. Stabilizing treatments, such as the heat-setting of nylon, have been introduced into industrial operation and constitute a practical recognition of strain and of behavior attendant upon such treatments. Information on recovery can also be helpful in attempting to understand the molecular mechanism responsible for fiber behavior, for any relaxation from deformation is simply a result of the action of forces within the fiber itself, and must find explanation solely in terms of those forces. A comparison of the behavior of fibers of different chemical composition, examined under similar conditions, can be of great assistance towards reaching such understanding. It was in order to expand our knowledge of the relaxation behavior of nylon, having regard for the practical as well as for the more theoretical usefulness of such information, that the present investigation was undertaken.

Fibers which have been stretched and released from tension show residual extensions which are dependent

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upon time, load, and the conditions under which the extensions and recoveries take place. In the present study, data on extensions and recoveries have been obtained for nylon filaments in air and in water. Where relaxation under the conditions which attended stretching does not result in complete recovery of the original unstretched length of the filament, further recovery can be effected by heat and swelling agents. Very little detailed investigation into induced recovery of this type has been carried out. The work of Leaderman [1] should be mentioned, but, except for this, references to such recovery have been made only in passing, or are not in sufficient detail to be of any real value. In order to augment the observations of Leaderman, all of which were made under very low stress, some experiments of this type were carried out on nylon.

The experimental measurements of extension and recovery were all made on single filaments of type 66, semi-dull nylon, free from oil and size, obtained from Canadian Industries Limited, Nylon Division.

Experimental Method

In order to ensure the use of filaments of constant average cross-sectional area, filaments were cut 19.0 in. long, conditioned at 65% R.H., and weighed individually on a sensitive torsion balance prior to mounting. Only those the weights of which lay in the range 16.5 ± 0.25 den. were used for further experiment. Since the internal strains which are introduced into a filament during manufacture are removed in varying degree by relaxation treatments such as those to be investigated, it was necessary to subject the test filament in each case to the same relaxing treatment before extending it as it was to receive after extension. In this way it was permissible to relate recovery brought about during the final relaxation treatments with strains introduced by the extension process.

The filament, *a*, was cemented at one end to a small stainless-steel hook, *b*, and at the other end to an assembly, *c*, consisting of a short length of stainless-steel wire, a piece of thread, and a wire loop (see Figure 1). A nitrocellulose-base cement was used on filaments to be extended in air, and an adhesive consisting of synthetic rubber suspended in a solvent was employed in the case of extensions in water.

Those filaments to be extended in air were conditioned for not less than 4 hrs. in a room operating at 65% R.H. and 70°F, and were then mounted in a glass tube, *d*, carrying a scale cemented to its outside wall. The bottom of the tube was closed by a rubber stopper, *e*, carrying a screw eye and a short piece of 5-mm. glass tubing. The hook attached to the lower end of the filament was inserted in the screw eye, and the thread at the upper end was led over a low-friction Bakelite pulley, *f*. When set up in this way the load on the filament (called zero load) was of the order of 1/100 g. per den. Filaments to be extended in water were conditioned by immersion in water at 70°F for not less than 2 hrs. prior to extension. The extension was carried out in the glass tube as described above. Water was introduced into or removed from this tube slowly through the small glass tubing at the bottom of the assembly in order not to disturb the mounted filament.

For observations of behavior under constant load, the appropriate weight, *g* (Figure 1), was applied by hooking it onto the wire loop at the end of the thread. The weights used were 5, 10, 20, 30, 50, or 60 g., corresponding to initial stresses of 0.303, 0.606, 1.21, 1.82, 3.03, and 3.64 g. per den. The addition of the weight was done smoothly over a period of something less than 1 sec. The weight was left hanging for the required length of time and

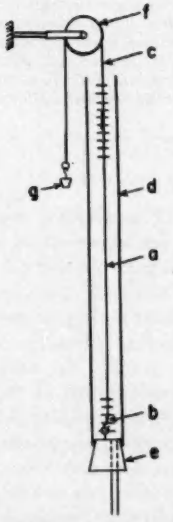

FIG. 1. *Apparatus for measurement of extension of single filaments under constant load.*

was then removed quickly but carefully so as not to jerk the filament. The intervals of time used were 30 sec., 10 min., 2 hrs., and 24 hrs. Readings of length were taken at intervals of 10, 30, 60, 180, 300, and 600 sec., and 2 or 24 hrs. after addition or removal of the load. Since the bottom of the filament was fixed, it was necessary to read its position only at the start of the experiment. Length changes were recorded from readings taken of the position of the upper end of the filament. Readings could be made to the nearest 1/100 in., with a maximum resultant error in length of 0.02 in. This represents an accuracy of ± 0.1%, which was considered sufficient for the purposes of the present investigation.

After removal of the load, the filament was allowed to relax for 24 hrs. This did not necessarily result in complete recovery, and an attempt was made to induce further relaxation by treatment with a swelling agent or with heat.

Those filaments which had been stretched and relaxed in air were given a relaxation treatment which consisted of one of the following: water at 21°C for 16 hrs.; steam at 121°C for 15 min.; dry heat at 160°–170°C for 5 min. Subsequent to this treatment the filament was again conditioned at 65% R.H., mounted in a tube, and its length measured.

Filaments which had been stretched and relaxed in water were subjected to one of the following treatments: 1% aqueous solution of *m*-cresol at 21°C for 5 hrs., followed by washings in ethyl alcohol and water; dry heat at 180°–190°C for 5 min. Following the treatment the filament was immersed in water for not less than 4 hrs., and its length measured.

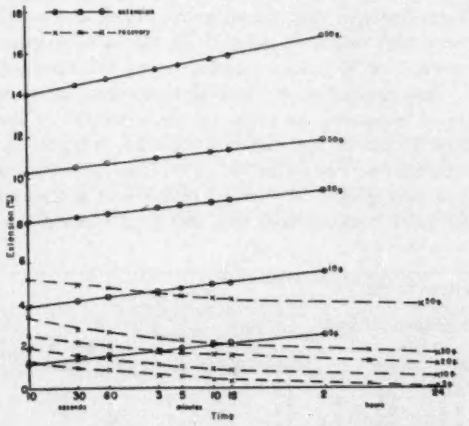

FIG. 2. *Extension and recovery curves (single-filament, 16.5-den. nylon) for 2-hr. loading period in air; 65% R.H.*

Experimental Results

Extension and Recovery in Air and Water

All measurements were made on filaments which had not previously been extended.

Typical extension and recovery curves are illustrated in Figure 2. These particular curves were obtained by applying each load in air at 65% R.H. for 2 hrs., and subsequently allowing the filament to relax for 24 hrs. under the same external conditions. The percentage extension produced by each load is plotted as a solid line against the logarithm of time, the scale of the latter running from 10 sec. to 24 hrs. The recovery is indicated by a dotted line, and in this case the abscissas refer to length of time after removal of load. For example, when a 30-g. load is applied to a filament, it extends 10.4% in 10 sec. After 2 hrs. it has extended 11.8%, at which time the load is removed. After an additional 10 sec. the extension has fallen to 3.4%, and 24 hrs. after removal of load it is only 1.6%. Results obtained on filaments held under load for different times, both in air and in water, provided curves with the same general features as those in Figure 2, and need not be discussed here.

Several characteristics of these extension curves are readily observable. The initial, rapid extension which takes place within the first 10 sec. after application of load increases with increase in stress, but not, so far as the range of stress being studied is concerned, in the simple manner of a Hooke's Law relationship. The extension which continues beyond the first recorded observation at 10 sec. is linear with the logarithm of time, and the slope of this line shows no appreciable difference for different loads up to 30 g. (1.8 g./den.). For a load of 50 g. (3.0 g./den.), however, it is distinctly greater, although there is no immediate departure of the linear relationship of extension with the logarithm of time. The recovery curves plotted in the same manner are not linear but appear to be closely parallel, regardless of the extensions from which recovery is taking place. The magnitude of the initial recovery is seen to be proportionately greater in experiments performed with

TABLE I. EXTENSION UNDER 30-.G LOAD

Length of time	Extension (%)
10 sec.	10.4
30 sec.	10.8
60 sec.	11.0
180 sec.	11.2
300 sec.	11.4
600 sec.	11.5
24 hrs.	12.4
40 hrs.	12.5
21 days	13.0
43 days	13.2
157 days	13.4
1 year	13.7

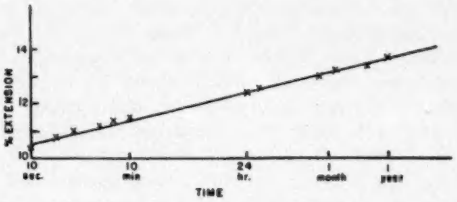

FIG. 3. *Long-term extension of single 16.5-den. nylon filament under 30-g. load.*

increasing load, but it is not immediately obvious to what extent this recovery is dependent upon the maximum extension produced while the filament was under stress.

These observations apply generally to all the extensions and recoveries measured, whether at 65% R.H. or immersed in water. In the case of extension in water, the magnitude of the rapid, initial extension is somewhat higher than in air at 65% R.H. under the same loading conditions, and the slower, delayed extension is again linear with the log of time, and the slope is independent of load up to 30 g. Moreover, this rate is not very different from the rate observed for filaments extended at 65% R.H. The recovery curves in water are similar in shape to those in air.

Extensions carried out over longer periods also proved to be linear with the log of time. Table I gives the results obtained by applying a 30-g. load to a filament in an atmosphere of 65% R.H. for a period of 1 year. These results are illustrated graphically in Figure 3.

A filament subjected to a 50-g. load was found to break after about 3 days. In this case the extension did not remain linear with log time, but after extensions of about 18% were reached, showed a gradually increasing rate up to break.

No single characteristic can be chosen which will represent completely the curves drawn from the experimental data. However, the extension curves, being linear, may be characterized by the extension in 10 sec. and the total extension reached after a specified time. The recovery curves are less readily described, but recovery data may be indicated satisfactorily for the present purpose by the extensions remaining in the filament after 10 sec. and 24 hrs. relaxation for each load and length of time giving rise to the deformation. These data are given in Tables II, III, and IV.

The term "air" in these tables refers to extension and recovery in an atmosphere of 65% R.H.; "water" means extension and recovery in water. All the work was done at a temperature of 70°F (21.1°C). The blanks in the tables indicate either that the filament broke or that the adhesive slipped due to the very high stresses (about 20 lb. per in. of circumference for 50 g. load), and no result was obtained.

An examination of Table II shows that the initial rapid extension, as given by the extension in the first 10 sec. of application of the load, is higher for filaments in water than in air, but the difference is not very great. The initial recovery of a filament in water is also greater than that for a filament sub-

TABLE II. EXTENSION (%)

Load	Time of application of load: 10 sec.		30 sec.		10 min.		2 hrs.		24 hrs.	
(g.)	Air	Water	Air	Water	Air	Water	Air	Water	Air	Water
5	1.2	2.4	1.4	2.6	2.0	3.1	2.6	3.6	3.0	4.0
10	3.9	4.8	4.2	5.2	4.9	6.1	5.6	6.7	6.1	7.2
20	7.9	8.6	8.2	8.9	8.8	9.8	9.4	10.3	10.0	—
30	10.3	11.2	10.6	11.6	11.2	12.2	11.8	12.9	12.5	—
50	14.0	15.7	14.5	17.6	15.7	22.1	16.8	—	17.8	—
60	16.0	20.6	17.5	25.5	—	—	—	—	—	—

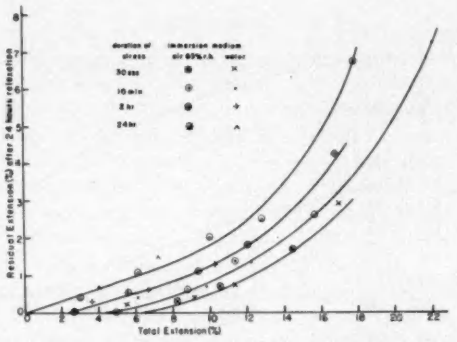

FIG. 4. *Relation between residual and total extension.*

jected to the same load for the same length of time in air. Except at the highest loads, the actual extension remaining after 10 sec. relaxation for a filament in water is as low or lower than for one in air, despite the total extension attained being higher in the former case. After 24 hrs. relaxation (Table IV), however, the residual extension in every case is as low or less in air than in water.

The relationship between the residual extension after 24 hrs. recovery and total extension is shown in Figure 4. For a given time of application of load, the points obtained from extension and recovery in air lie on the same curve as those obtained in water. In these two media at least, therefore, it is apparent that the degree of recovery in 24 hrs. depends only upon the total extension and time for which the filament was under load.

Recovery Induced by Heat and Swelling Agents

Each of the filaments which was to be relaxed by treatment with heat or a swelling agent was subjected to the same treatment before deformation as it was to receive after. In this way strains in the molecular structure existing in the original filament and capable of being removed by heat or swelling were eliminated, so that the final relaxation affected only those strains introduced during deformation. As might be expected, the extension characteristics of certain of these treated filaments differed in varying degree from those of an untreated filament. However, for the most part these differences were not sufficiently large relative to those which existed between individual untreated filaments to permit a statistically significant comparison to be made from the number of filaments observed. Therefore, the differences can only be described in general terms. Those filaments treated with dry heat remained essentially unchanged. Those treated with steam became slightly more extensible and, perhaps, recovered rather less than would be predicted from Figure 4, which refers to untreated filaments. Treatment with *m*-cresol increased the extension for each set of loading conditions markedly, and decreased the degree of recovery, as would be predicted from Figure 4, except for extensions of the order of 20% or over.

In order to determine whether the relaxation treatments used were causing permanent damage to the filaments, the effect of these treatments upon the breaking strength of 40-den., 13-filament, semi-dull nylon yarn was measured. In each case the yarn was subjected to exactly the same treatment as was to be used for relaxation, conditioned at 65% R.H., 70°F, and the breaking strength measured on a Scott IP–2 inclined-plane tester. The treatments used were: steamed at 15 lb. excess pressure for 15 min.; immersion in 1% aqueous *m*-cresol solution at 70°F for 5 hrs., followed by washing in ethyl alcohol and water; dry heat at 160°C for 5 min.; dry heat at 190°C for 5 min. The results are given in Table V, each figure given being the mean of 10 breaks.

None of these treatments caused a high loss in breaking strength, and thus it can be assumed that

TABLE III. RESIDUAL EXTENSION (%) AFTER 10 SEC. RECOVERY

Load (g.)	Time of application of load: 30 sec. Air	30 sec. Water	10 min. Air	10 min. Water	2 hrs. Air	2 hrs. Water	24 hrs. Air	24 hrs. Water
5	0.1	0	0.9	0.2	1.4	1.1	2.2	1.8
10	0.4	0.4	1.2	0.9	1.9	1.8	3.2	2.8
20	1.0	1.0	1.8	1.6	2.5	2.5	3.7	—
30	1.7	1.4	2.7	2.6	3.4	2.9	4.1	—
50	3.0	4.1	4.3	8.8	5.2	—	7.5	—

TABLE IV. RESIDUAL EXTENSION (%) AFTER 24 HRS. RECOVERY

Load (g.)	Time of application of load: 30 sec. Air	30 sec. Water	10 min. Air	10 min. Water	2 hrs. Air	2 hrs. Water	24 hrs. Air	24 hrs. Water
5	0	0	0	0	0.1	0.3	0.4	0.7
10	0	0.2	0	0.4	0.6	0.6	1.1	1.5
20	0.4	0.4	0.7	0.7	1.1	1.3	1.9	—
30	0.7	0.7	1.5	1.5	1.6	1.6	2.5	—
50	1.8	2.9	2.6	7.2	4.0	—	6.0	—

TABLE V. EFFECT OF RELAXING TREATMENTS ON BREAKING STRENGTH

Treatment	Breaking strength (g.)	Loss in breaking strength (%)
None	223	—
Steam, 121°C, 15 min.	216	3
1% *m*-cresol, 5 hrs.	204	8
Dry heat, 160°C, 5 min.	218	2
Dry heat, 190°C, 5 min.	196	12

rearrangement of the molecular chains had taken place without marked decrease in the adhesion forces between them.

The effect of the various heat and swelling relaxation treatments is summarized in Tables VI, VII, and VIII. Table VI refers to those filaments which were stretched and relaxed in air, and gives the amount of extension remaining after further treatment in water at 21°C, steam at 121°C, or dry air at 160°C, as described above. Table VII refers to filaments stretched and relaxed in water, and gives the residual extension after treatment in dry air at 190°C. Table VIII refers to filaments which had been preconditioned by soaking in 1% *m*-cresol solution, and gives the residual extension after stretching in water, followed by 24 hrs. recovery in water, as well as the residual extension after further treatment with 1% *m*-cresol solution. Because pretreatment of the filament with this reagent markedly changes its load-extension characteristics, the figures for total extension are also included in Table VIII.

In spite of the relaxation treatment given each filament before stretching, some recovered to a length shorter than the original unstretched length. This never amounted to more than a few tenths of a percent, however, and the result was not uniform from filament to filament. It is possible that it reflects a failure to relax the filament completely

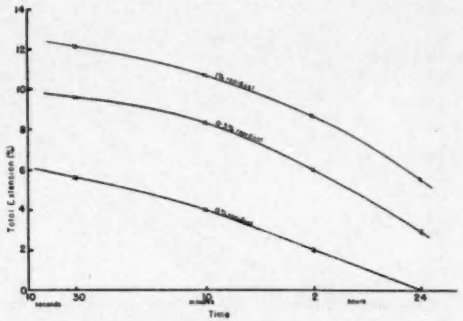

FIG. 5. *Relation between residual extension, total extension, and time.*

in the first treatment. All filaments which recovered their original length, as well as those which became slightly shorter, are therefore recorded as having zero residual extension, and it should be realized that the residual extension figures quoted are probably not accurate to better than ± 0.5%.

It can be seen that swelling, heat, or a combination of the two is capable of producing almost complete recovery in all the filaments extended in air except those which underwent considerable strain for a long time. Even for severe loading conditions —for example, a 50-g. load applied for 24 hrs.— recovery to within 2.6% of the original length was possible. The differences between the three relaxation treatments studied were not such as to indicate any one as being more efficient than the other two in effecting recovery.

Similar results were obtained with filaments extended in water. In this case both a more powerful swelling agent than water (1% *m*-cresol) and heat proved capable of causing a further reduction in the residual extension in the fiber. Of the two, however, dry heat was markedly more effective.

TABLE VI. RESIDUAL EXTENSION (%) AFTER RELAXATION TREATMENT FOR FILAMENTS EXTENDED IN AIR

	Time of application of load:											
	30 sec.			10 min.			2 hrs.			24 hrs.		
Load (g.)	Water, 21°C	Steam, 121°C	Air, 160°C	Water, 21°C	Steam, 121°C	Air, 160°C	Water, 21°C	Steam, 121°C	Air, 160°C	Water, 21°C	Steam, 121°C	Air, 160°C
5	0	0	0	0	0	0	0	0	0	0.1	0	0
10	0	0	0	0	0	0	0.1	0	0	0.2	0	0
20	0.1	0	0	0.3	0	0	0.4	0.1	0.1	0.7	0.1	0.9
30	0.1	0.1	0	0.4	0.1	0.4	0.7	0.5	0.2	1.1	0.2	1.0
50	0.6	0.8	0	1.1	1.5	0.8	2.1	1.8	2.2	2.6	2.9	3.9

Discussion

It is apparent from the results obtained that the extent to which a nylon filament will recover after being stretched depends not only upon the degree of stretch imposed but also upon the time of extension and recovery involved. This is a well-known behavior shared by all textile fibers. Because of this dependence upon time, no simple definition of "elastic limit" may be stated, and the common use of the term is often misleading.

This can be illustrated by an examination of the results for filaments stretched and relaxed in either air or water. The relationship between total extension and time for residual extensions of 0%, 0.5%, and 1% was read off from Figure 4 and plotted in Figure 5. If 24 hrs. is allowed for recovery, the curve for 0% residual extension describes the elastic limit of the extension in terms of the time for which the filament is extended. For example, if the filament is to be extended for only 30 sec., the "elastic limit," defined in this way, is almost 6%. If the duration of the extension is 10 min., the elastic limit falls to 4%; if 2 hrs., only 2%. If it is to be extended for 24 hrs. it will not recover completely from any appreciable extension. The "elastic limit" may be increased, of course, if a more rigorous relaxing treatment such as those described using heat or swelling agents is subsequently employed.

It is also an uncertain matter what residual extension, if any, can be considered as truly "nonrecoverable." It is clear from the experiments described above that what may be a permanent deformation under one set of recovery conditions may be reduced to zero under a different set of conditions. Moreover, since there is no reason to suppose that the relaxing treatments investigated are the best available, it cannot be assumed that any of the residual deformations observed would completely resist recovery under the most favorable conditions. It would seem, then, that the term "nonrecoverable" cannot be used with accuracy in connection with textile fibers without specifying the conditions under which recovery will not take place.

TABLE VII. Residual Extension (%) after Relaxation in Dry Air at 190°C for Filaments Extended in Water

Load (g.)	Time of application of load: 30 sec.	10 min.	2 hrs.	24 hrs.
5	0	0	0	0
10	0	0	0	0
20	0	0	0	0
30	0	0.1	0	1.7
50	1.2	—	—	—

Summary

The extent to which a nylon filament recovers after stretching under a constant load depends upon the total extension and the time under load, but is the same whether the extension and recovery are carried out in air at 65% R.H. or in water. Further reduction in the residual extension can be effected through the use of heat or swelling agents. Water at 21°C, steam at 121°C, or dry air at 160°C all serve to bring about a considerable further contraction in filaments which had previously been extended and relaxed in air at 21°C. In the case of filaments extended and relaxed in water, further contraction in length can be effected by treatment in air at 190°C or with 1% aqueous *m*-cresol solution at room temperature.

TABLE VIII. Total and Residual Extension (%) for Filaments Soaked in 1% *m*-Cresol, Extended in Water, and Relaxed in 1% *m*-Cresol

Load (g.)	Time of application of load: 30 sec. Total	Residual Water	Residual *m*-Cresol	10 min. Total	Residual Water	Residual *m*-Cresol	2 hrs. Total	Residual Water	Residual *m*-Cresol	24 hrs. Total	Residual Water	Residual *m*-Cresol
5	6.9	1.5	0.4	8.2	2.3	0.4	8.4	2.6	0.5	9.0	3.3	0.4
10	12.0	2.3	0.2	12.6	3.0	0.3	13.7	4.4	0.4	14.5	5.3	1.0
20	18.1	3.3	0.8	18.4	5.0	1.2	19.5	6.0	1.9	20.0	7.2	2.4
30	18.9	3.9	1.3	19.9	5.2	1.9	21.2	7.6	2.5	21.6	7.8	3.8
50	34.6	13.3	6.5	38.6	17.8	10.3	—	—	—	—	—	—

Acknowledgment

The author is indebted to Dr. A. C. Goodings for his helpful criticism, to Mr. R. B. Hadgraft and Miss Jean Parker, who carried out the measurements, and to Canadian Industries Limited, Nylon Division, the sponsor of this work.

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(Manuscript received November 16, 1950.)

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

"The Sub-Cuticle Membrane—A Recently Discovered Morphological Component of the Wool Fiber"

SWEDISH INSTITUTE FOR TEXTILE RESEARCH
Gothenburg, Sweden
October 20, 1950

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In the communication from Alexander and Earland [1], the authors claim to have "discovered an unobjectionable method for separating a membrane which may be identical with the 'subcutis'" earlier predicted by Reumuth *et al.* [4, 6, 7, 11, 12]. Further, Alexander and Earland write: "The membrane also is quite resistant to chlorine solutions of any pH, whereas if it consisted of scales held together by non-protein epicuticle it would collapse, since by this treatment the latter would be detached from the wool."

The membrane isolated by Alexander and Earland represents between 7% and 10% of the wool substance, according to their paper. The epicuticle represents approximately 0.1% of the wool, and it is therefore quite improbable that the epicuticle should be the bearing or cohering component of Alexander and Earland's membrane. The cohering, chlorine-resistant forces must be present deeper in the cuticle or the cortex layer, and thus the chlorine-resistance of the isolated material does not indicate that it should be free from epicuticle.

The membrane of Alexander and Earland is much thicker than the tube isolated earlier by Lehmann [6, 7] and by Elöd and Zahn [4], who used the same name of "subcutis." It has been shown in a paper from the Swedish Institute for Textile Research [9] that the Lehmann tubes originate from the surface of the fiber and consist of the outer part of the cuticle

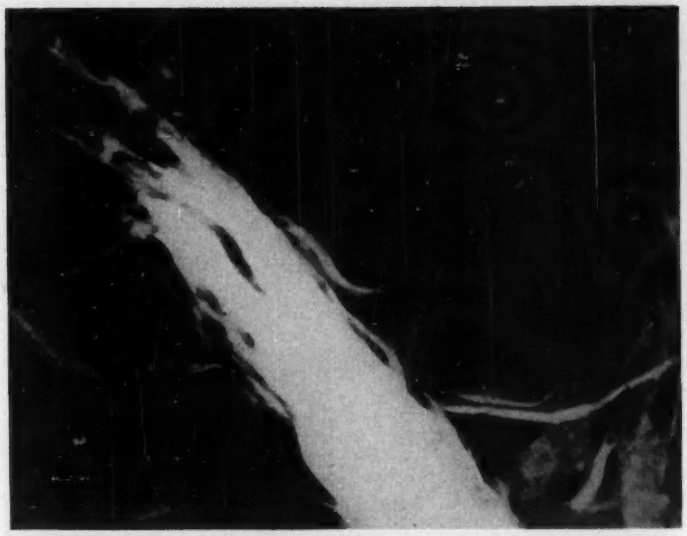

Fig. 1. *Photograph showing cortex cell splitting up into fibrils, and small pieces of epicuticle. Specimen was treated with ultrasonics and shadowed with Pd (4:1).*

Fig. 2. *Epicuticle from same specimen as that shown in Figure 1.*

—namely, the epicuticle—and the protein substance forming the layer closest to the epicuticle.

Zahn and Haselmann have shown [14] that the outer part of the cortex is chemically more resistant than the rest of the cortex. They have isolated this part of the cortex as a membrane after mechanical removal of the cuticle from horse hair, and have given the name "Zwischenmembran" to this struc-

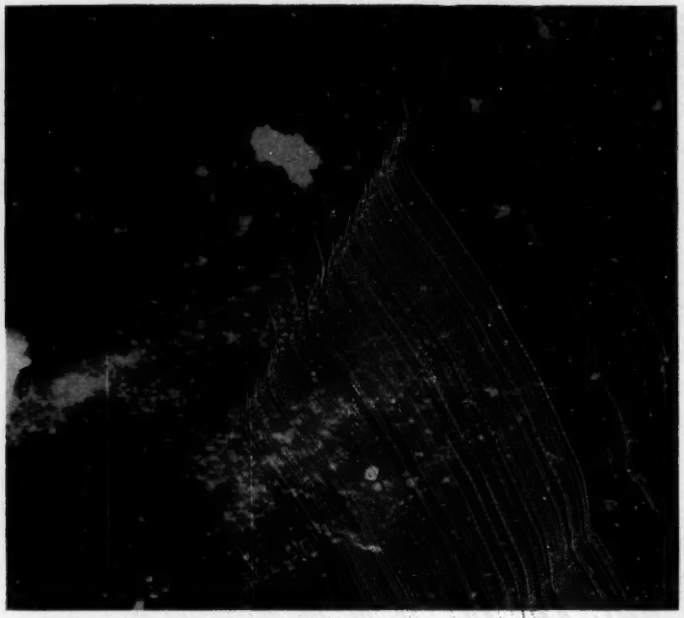

FIG. 3. *Epicuticle isolated by treating the sample shown in Figure 1 with dilute Na_2S solution. (Pd-shadowed (4:1).)*

ture. It should be observed that this "Zwischenmembran" is not identical with the Lehmann tubes.

On our request, Dr. Alexander kindly supplied us with a sample of the material isolated by him and his coworker. We have examined this sample in the electron microscope. Cortical cells, fibrils, and pieces of epicuticle were all found to be rather abundant. We also found pieces consisting of epicuticle thickened by adhering substance. Some pieces of the specimen were so thick that the electrons could not penetrate them or reveal their structure.

Figure 1 shows a specimen treated with ultrasonics and shadowed with Pd (4:1). The photograph shows a typical cortex cell splitting up into fibrils, and also small pieces of epicuticle. Figure 2 is of the same specimen, and shows a piece of epicuticle of the same type as can be isolated by chlorinating wool and shaking it in water [8]. When the material was treated with 1% Na_2S in water at 40°C for 5 days, pictures like that shown in Figure 3 were obtained. This residue has the same appearance and the same thickness as epicuticle isolated by treating wool with dilute Na_2S solution.

Our conclusion is that the preparation of Alexander and Earland consists of parts of the cuticle and the outer parts of the cortex. The sample seemed to be rather heterogeneous. The main part of it is probably the outer, resistant part of the cortex, which Zahn and Haselmann have isolated as their "Zwischenmembran." Nothing indicates that this membrane should be identical with the "subcutis" of Reumuth, Lehmann, and Elöd and Zahn, which originates from the surface of the fiber.

Our earlier critical investigation of the Lehmann tubes [9], which led to the conclusion that the cuticle consists of epi-, exo-, and endocuticle, is not contradicted by Alexander and Earland's and Zahn's new findings. The terminology used by them is rather confusing because it does not indicate that the membrane isolated by them is a new discovery, not identical with Lehmann's "subcutis."

NILS GRALÉN
GÖSTA LAGERMALM
BO PHILIP

Author's Comments

We would like to point out the large measure of agreement which now exists concerning the presence of a continuous membrane below the scales of the

wool fiber, and to emphasize that the disagreement has now been reduced to one of nomenclature. Professor Gralén and his colleagues agree that there is a protein membrane representing a substantial part of the fiber on the surface of the cortex which can be isolated either chemically, by oxidation of the fiber with peracetic acid followed by extraction with ammonia [1], or by mechanical sectioning [14]. Gralén *et al.* claim, however, that this is a new morphological component and not the membrane variously called "epidermis membrane" [11], "subcutis" [6], and "Zwischenmembran" [5], since they believe [9] that these are only layers of cuticular material stuck together by the epicuticle.* We have not examined preparations made by the method of Lehmann [6], and this discussion does not include these. We believe, however, that the membranes obtained by the following different methods of preparation are all identical:

(*a*) Wool fibers heated in formamide and enzymatically extracted [4];

(*b*) Wool treated in 2*N* NaOH [14] (hair treated in *N* NaOH [12]);

(*c*) Wool oxidized with peracetic acid and extracted with ammonia [1];

(*d*) Hair sectioned with a razor blade, followed by treatment in pancreatin in sulfuric acid [14].

In particular, a detailed optical comparison of preparations made according to methods (*c*) and (*d*) establishes their identity beyond doubt.

The samples of membranes obtained by methods (*a*) and (*b*) contain scales; these are referred to as "exo- and endocuticles" by Gralén *et al.* This was stated in the original publications and could be seen from the photomicrographs. The Swedish workers [9], finding cuticular material in the electron-microscopic pictures of these preparations, concluded that these were the only constituents. When considering this observation, it must be remembered that the electron microscope is not a quantitative tool, since it shows only a small fraction of the preparation after this has been disintegrated by ultrasonics, which would probably disperse the scales preferentially.

The membrane isolated from oxidized wool [1] can be seen from the published photomicrograph to be free from scales and to be made up of fibrils. Gralén *et al.* conclude from their electron-microscopic investigation that the membrane thus prepared is largely fibrillar in composition; the existence of a membrane distinct from the scales, which can be isolated chemically, is no longer disputed. The only difference remaining between the writers and Gralén *et al.* is therefore whether the earlier methods of isolation did in fact yield this membrane.

Gralén *et al.* detected in the membrane from peracetic-treated wool the presence of epicuticle, spindle cells, and thick places which were not transparent to electrons, and stated that this preparation is rather heterogeneous. It is not surprising that a chemical method does not yield an absolutely uncontaminated membrane from a starting material as complex as the wool fiber, and the very sensitive electron microscope can, of course, readily detect extraneous matter without, however, providing any information as to its quantity. The presence of epicuticle in the preparation is to be expected in view of its chemical inertness, and the possibility that the membrane was contaminated by it was suggested in the original paper [1]. Since the epicuticle can represent, at the most, 1.5% of the preparation, it cannot be considered as an important part of the membrane, and merely serves to illustrate the extreme sensitivity of the electron-microscopic investigation. One would not expect a membrane of the thickness found by us to be transparent to electrons, and only the disintegration with ultrasonics, which is unlikely to be complete, produces fragments thin enough for the electron microscope. There is thus no evidence on which it can be claimed that the membrane contains thick and thin portions. In fact, an investigation of our own with the membrane as it is isolated showed that no part of it transmitted electrons. It seems not unlikely that this is the reason why the Swedish workers [9] could only detect the adventitious impurities and not the membrane itself in the earlier preparations.

The morphological position is unambiguously established by the mechanical method of isolation [14], which proves that the membrane is histologically related to the cortex and can be considered as its outer layer. The work of Gralén *et al.* reported above supports this conclusion. The following observations made with the chemically isolated preparations

*It is important to point out that Müller [10] in 1939 detected microscopically a layer on the surface of the scales which was responsible for the Allwörden bubbles. It seems probable that the layer found by Lindberg, Philip, and Gralén in 1948 [8] in the electron microscope, called the "epicuticle," is the same as the Müller preparation.

show clearly that the membrane must be considered as a separate component of wool and hair:

(*a*) It can be isolated as a membrane by chemical treatments and remains, unlike the bulk of the fibers, insoluble in alkali cupriethylenediamine and lithium bromide [1] after all the disulfide bonds have been broken;

(*b*) Its amino acid composition is different from that of the fiber as a whole [2];

(*c*) The crystalline arrangement of the membrane *as isolated from the oxidized fiber* is different from that of the remainder of the fiber [2];

(*d*) The diffusion of anions in alkaline solution into a wool fiber is rate-controlled by the transport across a membrane near the surface of the fiber even when the epicuticle has been removed [3].

The early nomenclature of the membrane as "epidermis membrane" is undoubtedly misleading since it suggests a histological relationship with the cuticle, whereas in view of its fibrillar structure, it is more accurately considered as part of the cortex. As a result, we prefer to use in German the term "Zwischenmembran," which was first introduced by Elöd and Zahn [5]. In English the term "intermediate layer" might be used, but "subcuticle" is probably preferable so long as it is realized that the membrane bears no histological relationship to the cuticle.

We should like to express our appreciation to Professor Gralén for showing us his article prior to publication, and for the valuable and helpful interchange of ideas which we have had with him.

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(*January 9, 1951.*)

Additional Comments

Obviously, our experiments have convinced Alexander, Zahn, and Haselmann that the "membrane," "isolated" by means of peracetic acid oxidation, consists mainly of cortical cells, although it is heavily contaminated with cuticular material. The results of our experiments were submitted to Alexander in a letter of March 2, 1950. We have shown [9] that the membrane isolated earlier by Elöd and Zahn [4] originates from the outer parts of the cuticle. The disagreement of nomenclature therefore is as follows: Alexander, Zahn, and Haselmann want to give the same name to two different things which we want to keep separate. Their reason is that they "believe" these preparations to be identical—*i.e.*, they do not believe in our experiments, although they have not demonstrated that anything is wrong with them.

The name they choose for these two substances—the "subcuticle"—is almost identical with the name "subcutis," adopted by Lehmann for his preparation, which they exclude from their discussion because they have not examined it. Both Zahn [13] and we [9] have pointed out earlier the close relationship or possible identity between the Lehmann tubes and the tubes obtained by means of formamide and enzyme, according to Elöd and Zahn [4].

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(*January 22, 1951.*)

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INDUSTRIAL SECTION

Color Changes in Wool During Processing*

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Abstract

Color is an important physical property of wool fibers which can be defined with the aid of color-measuring instruments. The color of a fiber is a limiting factor in the range of shades into which the fiber can be dyed. Color changes which occur to the wool substrate itself during normal processing steps, such as scouring, carbonizing, bleaching, dyeing, steaming, drying, and others, are significant in terms of the resulting limitations imposed on the shades obtainable. The size of the reflectance-level changes occurring in these processes is given and related to changes in utility and value of the fiber.

COLOR is a physical property of fibers which ranks in importance with tensile strength, abrasion-resistance, wear, and others. With adequate color-measuring devices, such as the General Electric Spectrophotometer, it is possible to define color and its impact on the value of a fiber in more precise terms.

In general, the range of colors to which a given fiber can be dyed is dependent upon the component of the color contributed by the fiber itself. That is to say, the lighter the intrinsic color of the fiber, the greater the number of different shades to which it can be dyed. In general, within a given type of natural fibers having other properties equivalent, whiteness or lack of color represents higher value. This has been known and utilized for many years by mill-operating personnel.

In the case of wool, everything that happens to the wool—from its initial formation on the back of a sheep or goat, where forage, climatic conditions, and other environmental factors are significant, to the manufacturing processes, such as scouring, drying, dyeing, steaming, and others—affects its inherent color. Since this color is an important factor in the value and utility of the fiber, it is important to know these changes and to control them if possible.

Measurement of color with a G.E. recording spectrophotometer results in a curve giving reflectance as a function of wave length. In order to be of practical value, this curve must be related to color needs. A convenient method of doing this is to relate the curve for the wool substrate to the curve for the desired color to be dyed. When three or four standard dyestuffs are used, it is clear that in order for a given color to be obtainable on a particular wool, the spectrophotometric curve for that wool must lie above the curve for the standard color at all points. This is due to the fact that dyestuffs produce color by absorption of light, and hence the dyeing of wool with all but fluorescent dyes must result in a lowering of the curve. This principle gives us the necessary yardstick to relate color level and color change to fiber use requirements.

While in practice this yardstick may consist of

* The material in this paper was presented at the Fall Meeting of The Fiber Society, Washington, D. C., Sept. 13, 1950.

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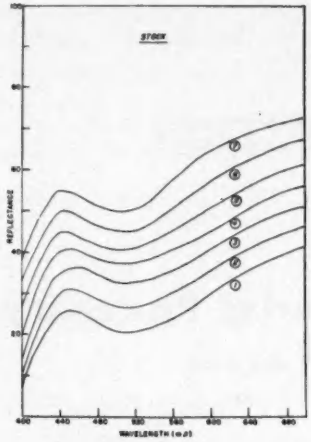


FIG. 1. *Spectrophotometric curves for seven reference stock-dyed shades.*

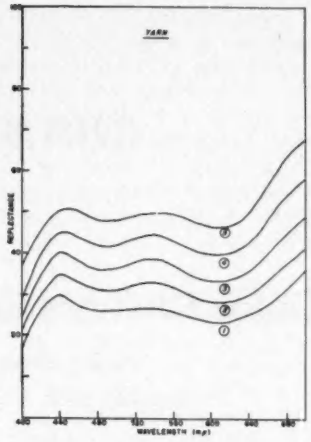


FIG. 2. *Spectrophotometric curves for five reference skein-dyed shades.*

the several hundred colors in a particular manufacturing line, for purposes of this discussion we use seven hypothetical shades on stock wool and five shades on yarns chosen so that they will define the color changes involved.

Figure 1 shows the spectrophotometric curves for the seven colors dyed on stock wool, while Figure 2 shows those for the five shades chosen as references for yarns.

If all colors to be dyed were dark ones and no brilliant, high-chroma shades were required, the problem would be practically nonexistent. However, today in many of the textile areas the desire is for very light pastels and brilliant shades. These require maximum whiteness in the wool substrate in order to be obtainable by standard dyeing techniques.

Wool first shows its color individuality while growing on the back of a sheep or goat. While heredity and breeding have an effect on the color of the fibers with regard to the amount of true pigment present, environmental factors have a lot to do with the color level of fibers as they enter the textile manufacturing operation. Among these, the wetness of the particular season has a large effect in producing a yellow color. Investigations carried out in Australia on canary stain, as this color is sometimes called, and reported by Lang [3], indicate that high temperatures and humidity play a vital part in its development. The shearing of the animals just prior to the rainy season in the summer offers some measure of control. In the case of South American wools, while differences in climate in local areas and different practices in protecting sheep from the elements almost mask the effect, it can be seen that BA Lambs and short second clips, which are March shearings following the South American summer season, are somewhat whiter than the long second clip, which is sheared in November after the usually wetter winter season. The average reflectance at 440 mμ of many shipments of BA Lambs is 55.0%, which allows the dyeing of all seven of the comparison curves shown in Figure 1. The second clip—short BA's—has an average reflectance at 440 mμ of 50.4%, which allows the dyeing of only six of the seven shades; while the longs, or November clip, averages 49.3% reflectance at 440 mμ, and thus allows only five of the seven shades to be dyed.

Another environmental factor is related to the silage and pasturage which the animal eats. A green color is found on the wool which shows interesting properties which are of appreciable consequence in production. The color can be extracted with solvent, as shown in Figure 3. There is little doubt of the relationship of this green color to chlorophyll, as evidenced by the curves in Figure 4 comparing the solvent extract of contaminated wool with that for grass.

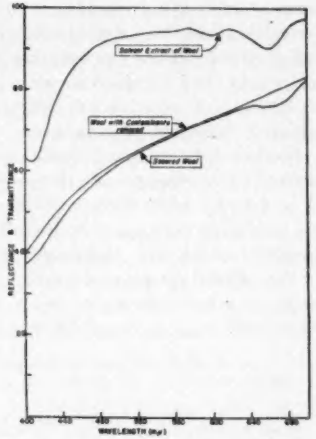


FIG. 3. *Colored contamination in wool.*

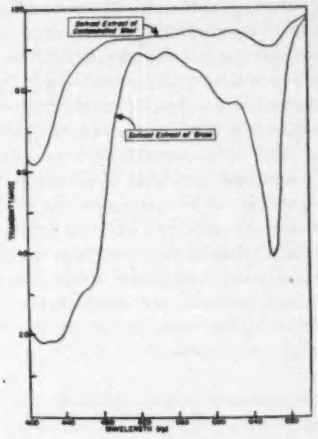


FIG. 4. *Relation of contaminant to chlorophyll.*

Wools, then, from many different areas and from different seasons, arrive at a textile producer's in a variety of states of color. Their color can be measured after a carefully controlled scouring procedure; as a result, each wool can be classified by reflectance using as a standard scale the reflectances of the wool required to dye a preselected group of shades. Wools of different casts can be blended to meet the reflectance-level requirements of the shades which must be dyed. The proportions of the blend can be predicted with good precision through the use of the Stearns-Noechel function [5]:

$$F = \frac{100 - R}{0.15(R - 1) + 1'}$$

where R is the reflectance in percent at any wave length and F is the function. Since F is proportional to the percent fiber present, the function can be used to calculate blends of any number of components by the following equations:

$$F_M = x_1F_1 + x_2F_2 + \ldots x_nF_n$$
$$x_1 + x_2 + \ldots x_n = 1,$$

where x_1 is the fraction of component 1 present and F_1 is the Stearns-Noechel function for that component at the chosen wave length. Table I shows how this technique can be used to predict the color of a wool blend.

TABLE I. CALCULATION OF BLEND COLOR BY STEARNS–NOECHEL EQUATION

Fiber	Fiber in blend (%)	x_nF_n
Wool type 1		
$R_1 = 57.2$ $F_1 = 4.539$	20	0.908
Wool type 2		
$R_2 = 43.6$ $F_2 = 7.632$	30	2.290
Wool type 3		
$R_3 = 52.5$ $F_3 = 5.444$	20	1.089
Wool type 4		
$R_4 = 48.5$ $F_4 = 6.338$	30	1.901
	100	$F_T = 6.188$
	Therefore:	$R_T = 49.5$

The first production factor which has a clear-cut effect on the color of the wool fibers is scouring. Obviously, the degree of scouring action or cleanliness of the wool influences its color. By scouring a wool more thoroughly, an appreciable reflectance increase can be obtained. The spectrophotometric curves for a yellowish blend of carpet wools after normal scouring and after extra-thorough scouring are shown in Figure 5. The normal scouring of stock allows for the possible dyeing of three of the

seven reference shades, while thorough scouring makes four of them obtainable.

In more precise terms, the degree of scouring action can be measured by residual grease content of the fibers and can then be correlated with color. At grease levels usually considered satisfactory, there is a fairly large amount of residual whiteness which is potentially available if better scouring were practiced. This correlation is shown in Figure 6. It can be seen from the reflectance levels involved that in order to dye all seven of the reference shades on this stock, very low grease content is required. These grease contents are much lower than the levels that heretofore were thought to be representative of good scouring quality.

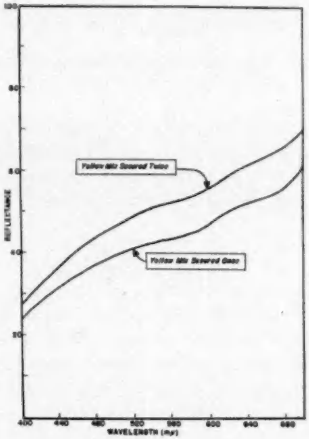


FIG. 5. *Effect of scouring on reflectance level.*

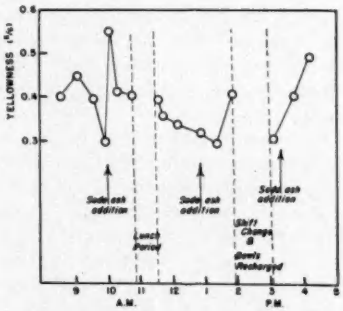


FIG. 7. *Production of yellowness by variations in scouring conditions.*

Color can be affected by scouring in other ways also. Excessive alkali, long drying, etc., produced by lack of control of either the scouring liquor or the rate of feed of wool, yield appreciable yellowing effect. A full day of scouring was followed colorwise. Figure 7 indicates that in every case the addition of soda ash to the bowl caused the wool to become appreciably yellower. Only those samples with $K/S < 0.45$ are white enough to dye the four darkest of the seven reference shades. The K/S values plotted indicate the degree of yellowness present in each of the samples measured.

By using a synthetic detergent scour at pH 7 and thereby eliminating all alkali drying effect, the

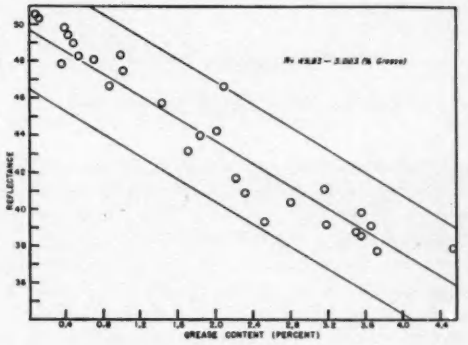


FIG. 6. *Relationship between grease content of scoured stock and reflectance level at 440 mμ.*

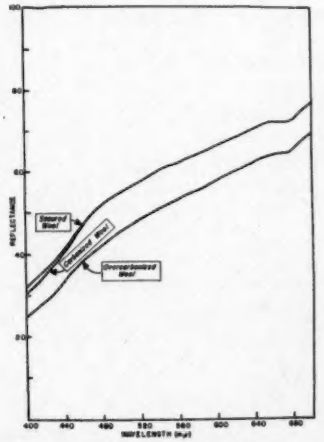


FIG. 8. *Color change on carbonizing wool stock.*

reflectance level of the clean stock leaving the dryer can be made even higher. The color level obtained through statistical quality-control techniques for a white carpet wool blend used for some time in manufacturing is 41.0% reflectance at 440 mμ. Neutral scouring with synthetic detergents raises this level to 49.9%. This represents a change from four to five reference shades which can be obtained on this wool blend.

In the case of carbonizing, the color change occurring in the wool is sensitive to the degree of severity of the treatment. Properly carbonized wool (Figure 8) shows little if any change in color. However, if an overtreatment occurs, the wool yellowing may be relatively severe, as indicated by the fact that only two of the seven reference shades can be obtained. The untreated and properly carbonized wools were light enough to allow four of the seven shades to be dyed.

Bleaching, of course, is designed to improve the reflectance level of the stock. In most cases, however, the degree of improvement immediately following a standard acid-peroxide bleach is not a good indication of the true bleaching action. Mock dyeing, which consists of carrying the fibers through a standard dye process with all chemicals but dye present, of the peroxide-bleached fibers shows that rather than yielding a true bleaching action, the wool substrate is actually as dark as, and in many cases darker than, the same stock would have been had it not been acid-peroxide bleached. Figure 9 shows the improvement in reflectance level obtainable by two acid-peroxide bleaching procedures. The single acid bleach is carried out with 15% hydrogen peroxide, pH 4.5; the yarn is squeezed to 104% pickup and dried at 250° F for 2¼ min. In the double acid-bleach process, the yarn was squeezed to 215% pickup and dried at 250° F for 4½ min. At this stage the curves indicate that the double bleach should allow the dyeing of all five skein shades, and the acid bleach should accommodate four shades. Upon mock dyeing, however, the difference in color change is surprising. In one case only two shades can be dyed and in the other only one of the five is possible.

On the other hand, if an alkaline process is used, which requires a much longer processing time, then part of the bleaching action is retained upon dyeing, as shown in Figure 10. If no change in inherent color occurred during dyeing, alkaline bleach would allow all five yarn shades to be obtainable; after mock dyeing, three of the five can be obtained, whereas only two could be obtained on the unbleached stock.

The wool substrate also changes color during acid dyeing. Again, the color change is primarily toward the yellow, as shown by a lowering of the reflectance level in the blue end of the spectrum. This color change becomes particularly evident when one attempts to use spectrophotometric curves

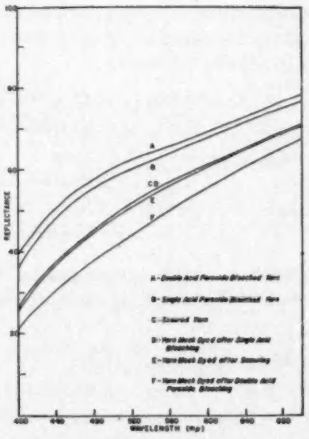


Fig. 9. *Color changes on bleaching and subsequent mock dyeing of woolen yarn.*

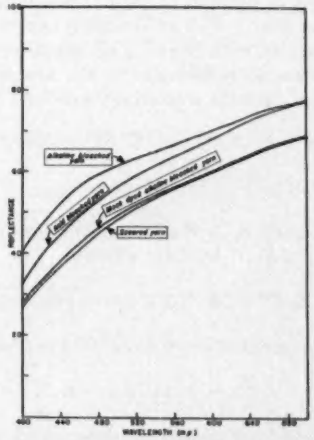


Fig. 10. *Color changes for alkaline-bleached yarn.*

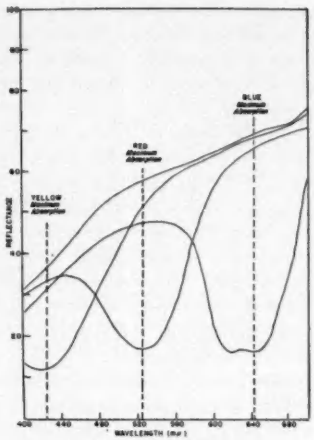


FIG. 11. *Spectrophotometric curves for yellow-, red-, and blue-dyed wool.*

to calculate the dyestuff recipe required to match a given shade. It is necessary, therefore, to define the color change of the wool substrate during dyeing and to correct formulations to account for the change.

We have developed a technique for shade matching along the lines described by Pineo [6], Stearns [7, 8], and Laughlin [4], which is based on the fact that the function K/S is proportional to the concentration of dyestuff or other coloring matter in or on the fiber. This relationship can be derived from the Kubelka-Munk [2] equation relating monochromatic reflectance to the absorption coefficient, K, and the scattering coefficient, S:

$$R = 1 + (K/S) - [(K/S)^2 + 2(K/S)]^{\frac{1}{2}},$$

where $K/S = \dfrac{1 - R^2}{2R}$.

If one corrects for the color of the wool substrate to obtain $(\Delta K/S)$ by subtraction:

$$(\Delta K/S) = (K/S)_{\text{dyed wool}} - (K/S)_{\text{wool}},$$

then the concentration of dye can be expressed as

$$C_D = a(\Delta K/S)_\lambda + b,$$

where a and b are empirically determined constants and $(\Delta K/S)$ is obtained at a wave length near the point of maximum absorption of the dye.

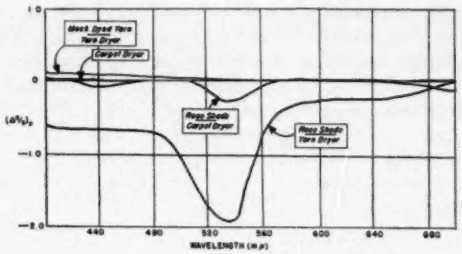


FIG. 12. *Color changes occurring during drying of yarns and carpets.*

In the simple case in which three dyes—red, yellow, blue—are used and in which the standard shade to be matched had been dyed with these three dyes, the calculation of dyestuff recipes is relatively simple.

It can be seen from Figure 11 that each dyestuff has maximum absorption points in different areas of the wave-length scale. It is obvious that while the contribution of each dye is largest at its own maximum absorption point, they also have some contribution to reflectance lowering at all points, including the maximum-absorption points of the other dyestuffs. It is true, therefore, that at any one wave length

$$(\Delta K/S)_{\text{total}} = (\Delta K/S)_{\text{yellow}} + (\Delta K/S)_{\text{red}} + (\Delta K/S)_{\text{blue}}.$$

It is possible, then, by doing calibration dyeings, to arrive at the following set of equations which can be solved by simple arithmetic:

$$C_Y = a_{YY}(\Delta K/S)_{YY} + b_{RY}(\Delta K/S)_{RY} + d_{BY}(\Delta K/S)_{BY} + e_Y$$

$$C_R = a_{YR}(\Delta K/S)_{YR} + b_{RR}(\Delta K/S)_{RR} + d_{BR}(\Delta K/S)_{BR} + e_R$$

$$C_B = a_{YB}(\Delta K/S)_{YB} + b_{RB}(\Delta K/S)_{RB} + d_{BB}(\Delta K/S)_{BB} + e_B.$$

A set of such equations worked out for Red 31M, Yellow 640, and Blue 1054 for skein dyeing are the following:

$$C_B = 36.7x - 0.366y + 12.60;$$
$$C_R = -8.46x + 30.8y - 0.0346z + 12.50;$$
$$C_Y = -0.552x - 3.14y + 24.2z - 1.95;$$

where $x = (\Delta K/S)_{\text{blue}}$, $y = (\Delta K/S)_{\text{red}}$, and $z = (\Delta K/S)_{\text{yellow}}$.

In determining the $(\Delta K/S)$ values, it is necessary to account for the wool yellowing during dyeing, which is of the order of 1.5%–2.0% and can be seen in the curve for one dip with skeins (Figure 9).

Recently, the General Electric Company has made available a cam for the spectrophotometer which performs the $\frac{(1-R)^2}{2-R}$ calculation automatically, as described by Pineo's patent [6], which, when used in conjunction with a special ruler, greatly simplifies these calculations. Considering the precision of this calculation, one may see by referring to Figure 9, which shows the color change of scoured wool on mock dyeing, that correction must often be made for this color change. Calculation of shade formulas, thereby reducing the number of dips required to obtain shade match, tends to make the color change less severe and hence extends somewhat the range of shades which can be dyed.

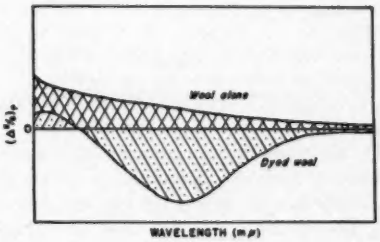
The dyed fibers must next be dried, and here, too, color changes occur which may be significant. Now that dyestuff is present on the fiber, the situation becomes more complex, for any one of all of the dyestuffs might change color for one reason or another, as might the wool itself. Using spectrophotometric techniques, however, these effects can be clearly separated and defined.

By obtaining a plot of $(\Delta K/S)_p$, the change in (K/S) occurring during the process, for the dyed fibers and for mock-dyed fibers which have had the identical treatment save the addition of dyestuff, against the wave length, it is possible to isolate the effects of the various potential components of color change. Figure 12 shows the changes which may occur during the drying of dyed skeins. It can be seen that the color changes occurring are related for the most part to dyestuff change and only to a fractional degree to wool-yellowing color change.

Using this technique, it is possible to define an index of fastness as a single number which, while it does not indicate the type of change occurring, is a function of the total change in amount of coloring material which has occurred (Figure 13).

The fastness index for dyed wool is graphically the area between the zero-change axis and the curve. The fastness index for the wool alone is the analogous quantity; while for the dye alone, it is necessary to obtain the area between the curves for wool alone and for dyed wool.

Stripping also has an important effect on color and color changes of the wool substrate. First of all, through stripping, waste and excess dyed fibers can be returned to the status of the basic wool substrate if a process such as Harristrip is used to insure against damage to the physical properties of the fiber. Although the color level of stripped stock is rarely as high as that for untreated new wool, it is of suitable level to be used efficiently in blends. Figure 14 compares the color level of



FASTNESS INDEX OF WOOL

$$(F.I.)_{ow} = \Delta\lambda \sum |(\Delta K/S)_{ow}|$$

FASTNESS INDEX OF DYED WOOL

$$(F.I.)_{ow} = \Delta\lambda \sum |(\Delta K/S)_{ow}|$$

FASTNESS INDEX OF DYE

$$(F.I.)_{ow} = \Delta\lambda \sum |(\Delta K/S)_{ow} - (\Delta K/S)_{w}|$$

FIG. 13. *Definition of fastness index.*

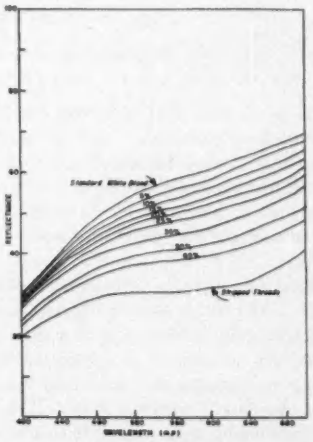


FIG. 14. *Color levels of white wool, threads stripped by the Harristrip process, and blends of the two.*

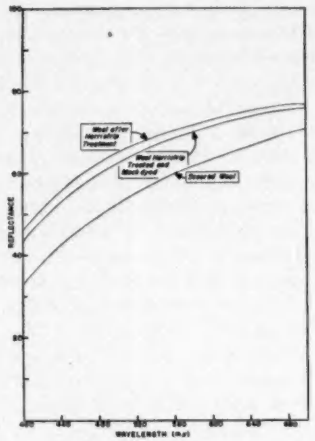


FIG. 15. *Effect of Harristrip on the wool substrate alone.*

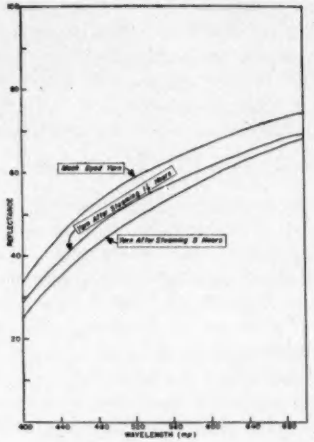


FIG. 17. *Changes in reflectance level produced by steaming.*

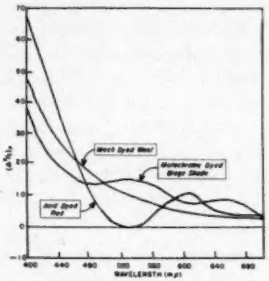


FIG. 16. *Typical color changes produced by steaming.*

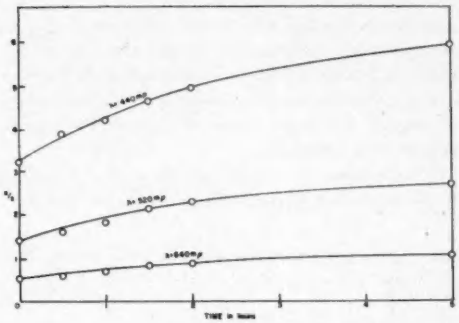


FIG. 18. *Color change as a function of steaming time.*

new white wool with that of stripped stock. The Stearns-Noechel relationship can be used to calculate by the technique indicated above the amount of such stripped fibers which can be added to a given white wool to produce a blend the reflectance level of which is suitable for the shades which are to be dyed on it.

The Harristrip process affects the color of the wool itself. As can be seen in Figure 15, a certain degree of bleaching action occurs which is apparently relatively permanent to subsequent redyeing.

Finishing operations on yarns and fabrics produce color changes in both the dyes and the wool at a stage in processing after which there is little if any flexibility to make corrections in color. To this extent, these changes cause the most difficulty, although they are not necessarily the largest in magnitude. Finishing operations involving steam, such as decatizing, steam setting, etc., are chief among the offenders. In this case, again, both the dyestuffs and the wool substrate are capable of undergoing changes in color. The technique of using $(\Delta K/S)_p$, the change in (K/S) during processing, is again useful in separating the components of the change. For $1\frac{1}{2}$-hr. steaming, changes may occur as indicated in Figure 16. Again, the dominant change in the wool color is in the direction of yellowness. It can be seen from Figure 17 that the color change is severe and that it also results in a lowering of the level of reflectance at all wave

lengths. At the start, the yarn was capable of dyeing three of the five yarn shades; after 1½ hrs. steaming, only two shades could be dyed; and after 5 hrs., only the darkest of the five shades would still be obtainable.

The rate of yellowing can be seen from Figure 18. It is apparently related to the yellowing in a boiling dye bath.

A few speculations can be made on the possible causes of this yellowing effect, which seems to be fairly universal for any conditions causing a degradation of wool color.

The absorption curve of a protein has typical absorption maxima in the ultraviolet region near the visible area of the spectrum which are associated with the aromatic nuclei in the protein from tryptophane, phenylalanine, and others. As ultraviolet radiation of the protein solution is allowed to occur, a brownish-yellow color appears due to the shift of these absorption bands in the near ultraviolet region into the visible region above 400 mμ. This new maximum is associated with quinone-type structures. It is possible, then, that the yellow color produced in wool which absorbs in the same area of the spectrum may be related to the formation of *o*-quinone structures from some of the aromatic amino acids present in the wool molecules.

Of course, in a general way, any type of reaction which could produce chromophoric groupings which absorb in the blue-violet region of the spectrum would produce the effects noted. Phillips has suggested that one of the chromophoric groups causing the yellow color in wool might be the disulfide group [1]. This idea explains nicely the fact that wool can be bleached by both oxidizing and reducing agents—hydrogen peroxide and sulfur dioxide gas. However, other processes, such as alkali treatment, which are known to cause disulfide-bond hydrolysis also cause appreciable wool yellowing. Therefore, while disulfide bonds may have a partial effect, a mechanism to explain all of the observed behavior must be more complex.

In conclusion, it is evident that although the reasons and mechanism for the color changes which occur are not understood, they are of vital significance in determining the utility of the fiber. Some color changes during processing have been recognized as such, but it has not been possible to define them and to realize their importance relative to the shades desired until the spectrophotometer and the techniques associated with its use were available.

Acknowledgment

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A Study of One-Step Conversion of Continuous-Filament Rayon to Spun Yarn*

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Abstract

The character and sources of denier nonuniformities in "direct-spun" yarn were investigated, and the variations were shown to be of two distinct types: long-length variations (10–100 ft. long) that arise from nonrandom breaking of the continuous filaments; and short-length variations (1–3 ft. long) that arise from discontinuous drafting of the broken filaments. The long-length variations, the more important of the two from the standpoint of fabric appearance, were found to result from minor variations in the tow or spinning machine which were greatly magnified by the spinning operation.

A simple modification of the direct spinner, known as the "angled, high-speed apron," was developed to control the breaking of the filaments over a short region near the input rolls. This simple change in the path and speed of the apron increased the average length of the broken filaments; increased the strength, elongation, and long-length uniformity of the yarn; improved the appearance of the fabric; and made possible for the first time the production of uniform, fine-count, direct-spun yarns. In order to be effective, the speed of the angled apron had to exceed a critical value that was shown to depend upon the front-roll speed and the position of the apron within the ratch.

FOR MANY YEARS, almost from the day that rayon was first manufactured, means have been sought for converting continuous-filament rayon into spun yarn. The method that has been most successful on a large scale and the one that is best known today is the process of cutting continuous-filament rayon "tow" into staple and processing it into spun yarn on conventional cotton-processing equipment. Since this conventional method involves the numerous steps of cutting, opening, baling, picking, carding, drawing, and spinning, considerable attention has been given to devising other methods that involve fewer steps. For example, a number of so-called "tow-to-top" processes have been developed [3, 5, 6] which transform the rayon "tow" into a "top" of discontinuous parallel filaments, thus substituting a single operation for all the conventional steps up through carding. Such tow-to-top processes, however, still retain the conventional drawing and spinning operations.

More recently, attempts have been made to develop one-step methods which would simplify the process of conversion even further by going directly from the tow to the spun yarn in a single breaking, drafting, and twisting operation. This so-called "direct-spinning" process (see Figure 1) was first developed about 10 years ago by the Saco-Lowell Company, which later manufactured a number of 204-position, direct-spinning frames and sold them. Many of these frames are today operating on a semicommercial basis with the object of defining the potentialities of the process. Already it has been shown that "direct-spun" yarns can be used in 100% "direct-spun" fabrics for a variety of uses and can also be used in combination with other

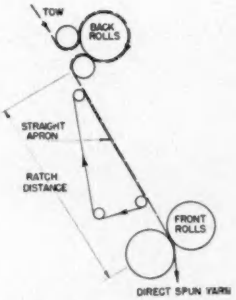

FIG. 1. *Schematic diagram of Saco-Lowell direct spinner.*

* Paper presented at the meeting of The Fiber Society, Lowell, Mass., Sept. 9, 1949.

TABLE I. Comparison of Direct-Spun Yarn with Conventional Staple Yarn

Direct-spinning process		Conventional staple process	
Tow: 4400 den.	1.5 den./filament	*Staple:*	1.5 den./filament
Approximate strength	3.8 g./den.	Approximate strength	2.4 g./den.
*Direct-spun yarn**	50's count	*Spun rayon yarn*	50's count
Average fiber length	7 in.	Average fiber length	1½ in.
Strength	2.0 g./den.	Strength	1.3 g./den.
Elongation	4.9%	Elongation	7.2%
Lea count	1840	Lea count	1300

* Direct-spinner settings: back-roll speed = 7.55 in./min.; front-roll speed = 317 in./min.; spindle speed = 6,730 r.p.m.; ratch distance = 12 in.; draft ratio = 42.

yarns to produce fabrics with unusual and desirable characteristics. It appears, therefore, that the direct-spinning process has many interesting possibilities.

In direct spinning the continuous-filament rayon tow is fed slowly into a pair of holding or "back rolls," and is broken and drafted by a second pair of "front rolls" moving at a higher speed. The ratio of the front- to the back-roll speed is called the "draft ratio," and the distance between the rolls is called the "ratch distance." The individual filaments break more or less at random over the entire ratch, so that there is a very broad distribution of fiber lengths—from very short fibers to fibers that are roughly equal in length to the ratch distance. Since the broken ends are distributed over the entire ratch, they must be supported and assisted into the nip of the front rolls. On the present commercial direct-spinning frames [1] this is accomplished by a straight leather apron driven at the speed of the back rolls (see Figure 1). Immediately beyond the front rolls the broken filaments are twisted together to form the direct-spun yarn.

A few results are given in Table I to illustrate the type of yarn properties that can be obtained on such a direct spinner. Starting with a tow having a total denier of 4400 and 1.5 den./filament, a 50's count yarn can be spun by using a draft ratio of 42. This is equivalent to spinning a 108-den. yarn. In general, spinning is carried out with a ratch setting of from 12 to 13 in., giving an average fiber length of approximately 7 in. Although the yarn elongation is somewhat lower, both the strength and lea count of the direct-spun yarn are considerably greater than those of a typical conventional-spun rayon of the same count (see Table I). This improvement in strength is not caused solely by the type of process itself, but is due in part to the greater strength of the original rayon fibers.

The direct-spinning process, however, is not without its inherent difficulties, the foremost of which are the erratic and generally severe variations in denier along the length of many direct-spun yarns. At present these variations in denier seriously limit the range of fine-count yarns that can be spun commercially, and they show up in fabrics as characteristic streaks and bands. This effect is illustrated in Figure 2 with samples of tubular-

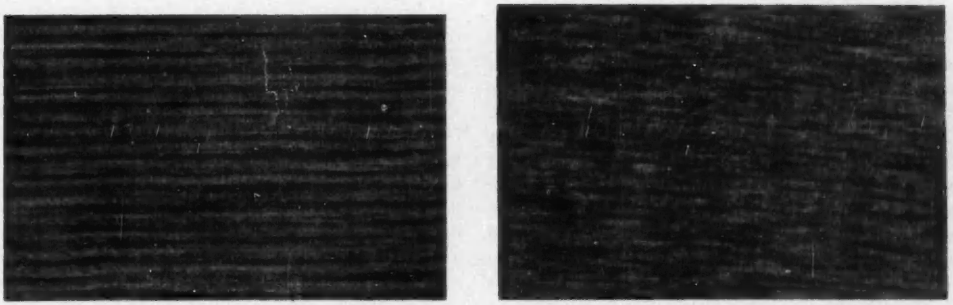

Fig. 2. Left—*Single-end knit tubing of direct-spun yarn.* Right—*Knit tubing control of conventional-spun rayon.*

knit fabrics made from direct-spun yarn and a conventional-spun rayon control. The direct-spun yarn variations are quite pronounced in comparison to the even appearance of the control. (This technique of using simple knitted fabrics instead of more complex fabrics for estimating uniformity was found to be quite useful.) It is obvious that for the majority of textile uses, including all flat fabrics and excluding only certain novelty goods, such yarn variations are undesirable.

At the beginning of this study very little was known about the origin and character of these variations in denier, and there was practically no information on the theory of the direct-spinning process in the literature. The present work was therefore aimed at understanding the fundamentals of the process and uncovering means for reducing the serious yarn variations to the low level obtained by the conventional process.

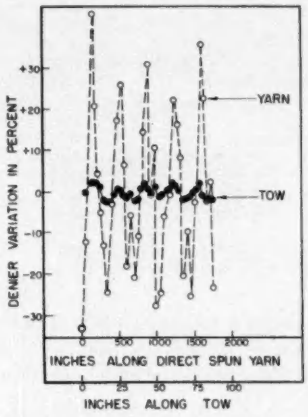

FIG. 3. *Magnification of tow variations by the direct-spinning process.*

Theory of Yarn Variations

A study of these yarn variations showed that they could be classified into two distinct types: long-length denier variations (of the order of 10 to 100 ft. long), and short-length denier variations (of the order of 1 to 3 ft. long). These two types of variations not only differed in length, but they also stemmed from entirely separate mechanisms and apparently were caused by different variables. Although the short-length variations in the direct-spun yarn did influence both the yarn strength and the spinnability, they were generally of the same magnitude as the short-length variations commonly found in conventional staple yarns—cotton as well as rayon [2]. Accordingly, the short-length variations were judged to be of lesser importance and attention was devoted mainly to an investigation of the long-length variations.

These long-length denier variations in the yarn were shown to result from nonrandom breaking within the ratch. That is, at a given instant the fibers broke with greater frequency at one part of the ratch than they did at another; a moment later the breaks occurred predominantly at some other part of the ratch. This change in breakage from one part of the ratch to another produced a variation in the average number of ends that were fed into the front rolls as a function of time. Any small variation in the tow or spinning machine that involved nonrandom breaking was found to be greatly magnified by the direct-spinning operation. For example, an experimental tow was made which contained a pronounced periodic variation 16.8 in. in length (see Figure 3). This tow variation caused a greatly magnified denier variation in the direct-spun yarn (obtained by weighing consecutive short lengths). The periods in the tow and yarn differed by the amount of the draft ratio, 21.4; while the amplitude was magnified from 1.3% to 18.8%. (It should be pointed out that a variation in denier as small as 1.3% is normally a negligible factor as far as continuous-filament rayon is concerned.)

The extent of this tow-to-yarn magnification was found to depend to a large degree upon the ratch distance. This is seen in Figure 4, where the period of the yarn variation was constant, since the draft ratio was constant, but the long-length amplitude was reduced more than five-fold when the ratch was decreased from 17½ in. to 4 in. Let us consider the reason why this change in ratch distance had such a great effect on the amplitude of the long-length yarn variations. When the ratch distance was short (4 in.) compared to the period in the tow (16.8 in.), the denier within the ratch was either all large or all small at any given instant; hence, the fibers broke more or less at random. On the other hand, in the case of the long ratch distance, the denier was both large and small within the ratch at a given time; hence, the fibers did not break at random but broke predominantly in the region of low denier. These considerations suggested that a relationship should exist between the ratch distance,

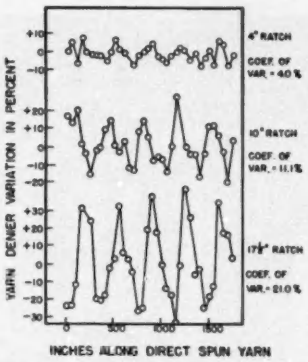
YARN DENIER VARIATION IN PERCENT
4" RATCH
COEF. OF VAR. = 4.0 %
10" RATCH
COEF. OF VAR. = 11.1 %
17½" RATCH
COEF. OF VAR. = 21.0 %
INCHES ALONG DIRECT SPUN YARN

FIG. 4. *Effect of ratch distance on magnification of tow variations.*

D, the period in the tow, λ, and the resulting magnification from tow to yarn. It was found possible to express this relationship mathematically as follows:

Let us consider a point X in the tow as it enters the ratch. If we let N_X be the number of filament breaks, expressed as breaks/in., that occur at X as it moves a distance dX, then N_X will depend upon the denier of the tow for the ratch distance, $X + D$, in front of X. As X progresses through the ratch, N_X will also depend upon the denier of the tow for the same distance, $X - D$, behind X. Furthermore, if we let N_A be the average number of breaks/in. that occur within all elements of the ratch during the time that X is in the ratch, then N_A will depend upon the average denier of the tow

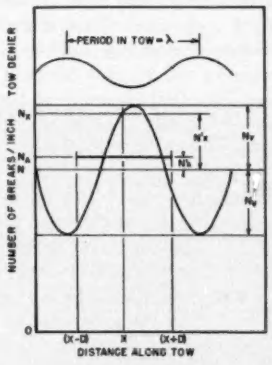

FIG. 5. *Sketch showing the variation in denier and the corresponding variation in the number of breaks/in. along the tow.*

over the interval $X - D$ to $X + D$. If the fibers are uniform within the ratch, N_X will be equal to N_A, and the breaks will be uniformly distributed. If N_X is not equal to N_A, the breaks will not occur uniformly. We wish now to consider this latter case and derive an expression for the following difference: $\dfrac{N_X - N_A}{N_A}$.

First of all, we assume a single periodic variation in the tow denier of length λ (see Figure 5); and, corresponding to this, we assume an inverse variation in the number of breaks/in. having the same period, λ, and a maximum amplitude, N_V, from the average number of breaks/in., N, for the entire length of tow. We now let N_X' be the variation from the average, N, at the point X; referring to Figure 5, we have these relations:

$$N_X' + N = N_X \tag{1}$$

$$N_X' = N_V \sin \frac{2\pi X}{\lambda}. \tag{2}$$

Since the average number of breaks/in., N_A, for the particular interval $X - D$ to $X + D$ differs from N by an amount equal to N_A' (see Figure 5), we also have the following relation:

$$N_A' + N = N_A, \tag{3}$$

with the average given by the integral:

$$N_A' = \frac{1}{2D} \int_{X-D}^{X+D} N_X' dX. \tag{4}$$

From equations (1) and (3):

$$\frac{N_X - N_A}{N_A} = \frac{N_X' - N_A'}{N_A}. \tag{5}$$

Substituting equations (2) and (4) into equation (5) and integrating for the desired difference, we obtain:

$$\frac{N_X - N_A}{N_A} = \frac{N_V}{N_A}\left[1 - \frac{\lambda/D}{2\pi} \sin \frac{360°}{\lambda/D}\right]. \tag{6}$$

If $N_A \cong N$, then $\left(\dfrac{N_V}{N_A}\right) \cong \left(\dfrac{N_V}{N}\right)$, which is proportional to the maximum variation in the tow; since $\left(\dfrac{N_X - N_A}{N_A}\right)$, the variation in the number of broken ends/in., is the assumed cause for the

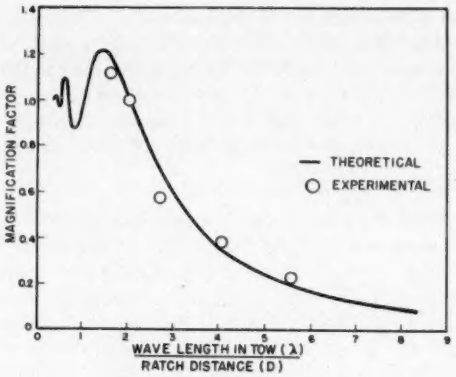

FIG. 6. *Theoretical magnification factor for the direct-spinning process.*

long-length variation in the direct-spun yarn, we have the following relation:

$$\% \text{ variation (yarn)} = \% \text{ variation (tow)}\ K\left[1 - \frac{\lambda/D}{2\pi}\sin\frac{360°}{\lambda/D}\right]. \quad (7)$$

Equation (7) shows that the amplitude of the long-length variation in the yarn is equal to the amplitude of the tow variation multiplied by an empirical constant, K, and by a so-called "magnification factor": $\left[1 - \frac{\lambda/D}{2\pi}\sin\frac{360°}{\lambda/D}\right]$. This factor is plotted in Figure 6 as a function of the ratio λ/D. The theoretical curve agrees quite well with the experimental points obtained from Figure 4. It has been necessary to use only the one empirically determined constant, K, which in this case is 14.5. While a tow denier variation was selected for this study, it should be apparent that any variable that causes nonrandom breaking within the ratch should cause long-length variations in the spun yarn.

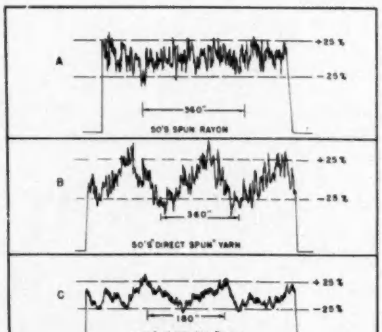

FIG. 7. *Uniformity charts for a spun-rayon control and for two direct-spun yarns.*

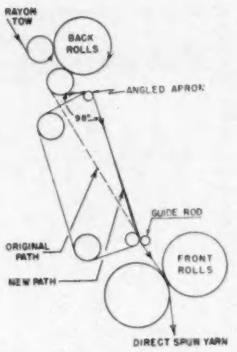

FIG. 8. *Diagram of the angled, high-speed apron direct spinner.*

When attention was turned from the effect of ratch distance to the effect of draft ratio, it became necessary to provide some means for analyzing long lengths of yarn (100 ft. or more) over relatively short intervals (several inches). Such an analysis would obviously be extremely tedious with the short-length denier method (see Figure 3); hence, an automatic yarn analyzer was needed. An instrument was developed which recorded the tension required to extend the spun yarn a fixed amount (draft ratio = 1.03) and good correlation was obtained between this tension and the actual measured denier of the yarn. This instrument was originally patterned after one used by Martindale [7] for measuring the tension between a pair of drafting rolls; however, in its final form the instrument was practically identical to the Frenzel-Hahn Universal Yarn Tester developed in Germany [8].

Figure 7 shows the uniformity charts for several yarns analyzed with this instrument. Figure 7*A* shows a chart for a 50's spun rayon used as a control; 7*B* shows a chart for a 50's direct-spun yarn made from a 2200-den. tow using a draft ratio of 21.4; 7*C* shows a chart for a 25's direct-spun yarn made from the same tow by merely reducing the draft ratio to 10.6. The parallel dash-lines at $\pm 25\%$ point out the fact that the amplitude of the long-length variation was independent of the draft

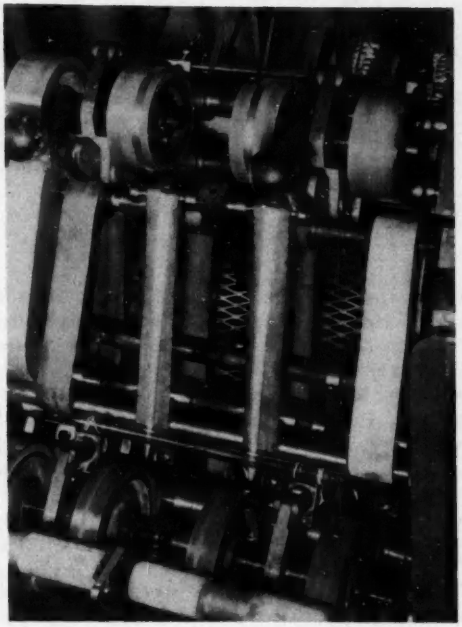

Fig. 9. *Photograph of the experimental angled, high-speed apron.*

ratio, which is in sharp contrast with the effect of the ratch distance (see Figure 4). Thus, it appeared that the draft ratio had no effect on where the filaments broke but merely spread the broken filaments over a longer length of spun yarn.

The uniformity charts of Figure 7 also show the presence of short-length denier variations superimposed on the long-length variations, which is worthy of comment. It is seen that the amplitude of these short-length variations increased markedly with draft ratio, although the amplitude of the long-length variations did not, implying that the short-length variations stemmed from some different source. Since these short-length variations were similar to the variations encountered in the conventional system (see Figure 7), it is believed that they were caused by irregular feeding of the broken ends into the nip of the front rolls.

Angled, High-Speed Apron Direct Spinner

Since it appeared that the long-length variations could be reduced by a shortening of the ratch, and the short-length variations were not too important from the standpoint of fabric appearance, the question might well be asked: Why not simply employ a short ratch to obtain the desired level of uniformity? The answer is that the reduction in average fiber length that accompanied the reduction in ratch reduced both the spinnability and the strength of the spun yarn, despite the improvement in uniformity. What was desired was some practical means for breaking the filaments over a short distance for the sake of uniformity, and at the same time obtaining long fibers for high strength and good spinnability.

One means for accomplishing this was developed during this work, which involved a change in the apron design. A diagram of this modification (the "angled, high-speed apron") is given in Figure 8, and a photograph of the experimental setup is shown in Figure 9. By diverting the path of the tow within the ratch over an angled surface moving at high speed, the breaking was restricted largely to

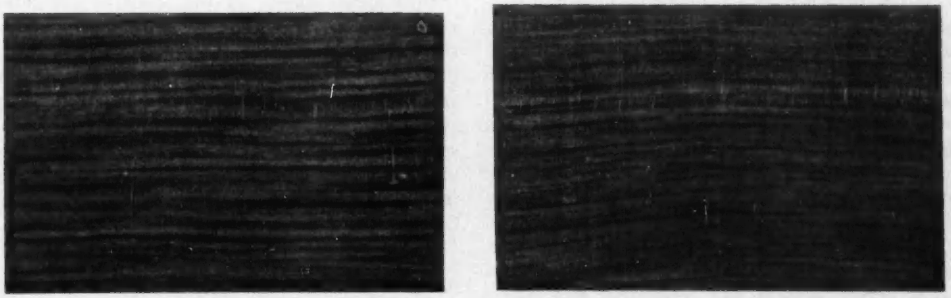

Fig. 10. Left—*Knit tubing of a 50's yarn spun with the straight apron.* Right—*Same yarn spun with the angled, high-speed apron.*

TABLE II. YARN PROPERTIES USING ANGLED APRON DIRECT SPINNER

	Direct-spinning process		Conventional staple process
	Straight apron	Angled apron*	
Count	50's	50's	50's
Den./filament	1.5	1.5	1.5
Average fiber length	7 in.	12 in.	1⅛ in.
Dry strength	2.0 g./den.	2.6 g./den.	1.3 g./den.
Elongation	4.9%	6.2%	7.2%
Lea count	1840	2800	1300

* Speed of angled apron = 340 in./min.

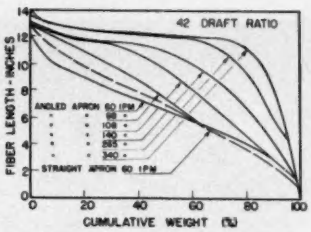

FIG. 11. *Effect of angled-apron speed on fiber length.*

the zone between the back rolls and the apron angle. This rather simple modification to the conventional direct spinner gave the desired long fibers broken over a comparatively short distance and greatly improved all of the important yarn properties. Foremost among these was the improvement in the long-length yarn uniformity and fabric appearance. Note the comparison in Figure 10 between the knit tubing made from yarn spun on the straight-apron direct spinner and the same-count yarn spun with the "angled apron." The long-length uniformity was markedly improved to a level approaching that of the conventional-spun rayon control (see Figure 2). Furthermore, the yarn showed a decided improvement in strength partly because of the increase in fiber length, and partly because of the increase in uniformity (see Table II). The strength of 50/1 direct-spun yarn was increased from 2.0 to 2.6 g./den. and the lea count improved from 1840 to 2800 through the use of the angled apron.

In addition to improving the strength and uniformity of the spun yarn, the angled, high-speed apron made possible the spinning of very fine yarns of acceptable uniformity and weavability. For example, with the angled, high-speed apron a 90/1 yarn was direct-spun from a 4400-den. tow, twisted to a 90/2 yarn, and woven into an experimental fabric which had the unique combination of high strength, good uniformity, and a very soft and pleasing "hand." This example of a 90/1 yarn spun with the angled apron marks a major advance from the 60/1 yarn which is the finest obtainable at present with the conventional straight-apron direct spinner. Because such fine-count rayon yarns are commerically difficult to spin by other methods, it appears quite possible that the angled apron direct spinner will ultimately find useful application in this field of fine-count yarns.

It is interesting to note that improvements in yarn properties were obtained only when the apron speed exceeded a certain "critical" value. This is best illustrated by a plot of the fiber length distribution as a function of the apron speed (see Figure 11). At low apron speeds there were actually fewer long fibers than with the straight-apron control. It was not until the critical apron speed was exceeded that a predominance of long fibers was obtained. For example, by using an apron speed of 340 in./min., 80% of the fibers were 12 in. in length or longer, and major improvements in both strength and uniformity were obtained (see Table II).

These striking effects of the speed of the angled apron indicated that the critical speed was some function of the various machine settings, and an equation was derived to express this relation mathematically.

Let us first consider the case of a single filament that is gripped between a pair of rolls and broken. During the instant of breaking, there must be a distribution of velocity along the filament since one end moves at the speed of the back rolls and the other end at the speed of the front rolls. The particular speed of the filament at the point of application of the angled apron is postulated as the critical apron speed. If the speed of the intermediate surface of the angled apron is higher than the speed of the fiber at that point, a slight additional tension should be imparted to the filament above the apron; the break, therefore, should occur above it. The equation for this critical apron speed as a function of the elongation of the filament to break is derived from the equation for the elongation of a staple fiber which was first derived in Germany at the Lehr Spinnerei [4].

The equation for a staple fiber is:

$$E(\%) = \left[\frac{V_2/V_1}{1+\left(\frac{V_2}{V_1}-1\right)_{\bullet}-\frac{V_2(L-D)}{V_1 D}}-1\right]100, \quad (8)$$

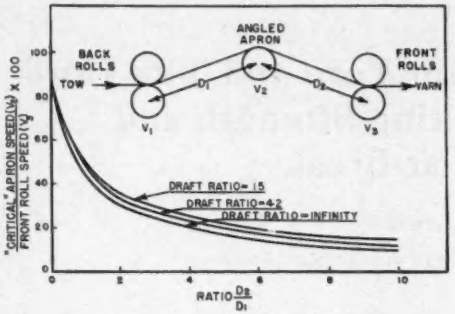

FIG. 12. *Theoretical critical speed of the angled apron.*

where E = maximum fiber elongation, L = fiber length, D = ratch distance, V_1 = back-roll speed, V_2 = front-roll speed.

The time, T, for the fiber to reach its maximum elongation is given by

$$T = \frac{L - D}{V_1}. \tag{9}$$

Substituting equation (9) into equation (8), we get:

$$T = \frac{D}{V_2}\log_e\left[\frac{V_2/V_1 - 1}{\dfrac{V_2/V_1}{E/100 + 1} - 1}\right]. \tag{10}$$

Consider the case where the angled apron divides the ratch into two zones (see Figure 12), and note the following new definitions: D_1 = distance from back rolls to angled apron; D_2 = distance from angled apron to front rolls; V_1 = back-roll speed; V_2 = critical apron speed; V_3 = front-roll speed; T_1 = time to break between V_1 and V_2; T_2 = time to break between V_2 and V_3.

T_1 and T_2 can be calculated separately from equation (10), and when the fiber speed equals the critical apron speed, $T_1 = T_2$; or:

$$\frac{D_1}{V_2}\log_e\left[\frac{V_2/V_1 - 1}{\dfrac{V_2/V_1}{E/100 + 1} - 1}\right] = \frac{D_2}{V_3}\log_e\left[\frac{V_3/V_2 - 1}{\dfrac{V_3/V_2}{E/100 + 1} - 1}\right]. \tag{11}$$

From equation (11) we derive our final equation:

$$V_2 = \frac{V_3\log_e\left[\dfrac{V_2/V_1 - 1}{\dfrac{V_2/V_1}{E/100 + 1} - 1}\right]}{D_2/D_1\log_e\left[\dfrac{V_3/V_2 - 1}{\dfrac{V_3/V_2}{E/100 + 1} - 1}\right]}. \tag{12}$$

TABLE III. CRITICAL SPEED OF ANGLED APRON

Ratio D_2/D_1	Draft ratio	Critical speed* Theoretical (in./min.)	Experimental (in./min.)
2.55	15	103	108
2.55	42	94	88

* Front-roll speed = 317 in./min.

The theoretical critical apron speed is plotted in Figure 12 as a percentage of the front-roll speed and as a function of D_2/D_1 for draft ratios of 15, 42, and infinity. It is shown that the critical speed is practically independent of the draft ratio and dependent almost entirely upon the front-roll speed and the position of the angle within the ratch.

This equation was checked experimentally using two widely different draft ratios of 15 and 42, and excellent agreement was obtained between the theoretical and experimental results (see Table III).

Further calculations using equation (12) showed that the breaking elongation should have practically no effect on the critical apron speed, and that neither the angularity of the apron nor the coefficient of friction between the apron and the fiber should have any effect on the critical speed, although they should affect the amount of tension transferred once the critical speed is passed. Experiments with the angled apron indicated that these calculated results were basically correct.

Acknowledgment

The authors express their appreciation to V. S. Van Scoy of the Rayon Department of the Du Pont Company, particularly for his contributions to the development of the "angled, high-speed apron" direct spinner.

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On Preconditioning Cotton Yarn and Tire Cord Before Testing Breaking Strength and Elongation-at-Break

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THE TESTS reported herein were made in order to learn to what degree breaking strength and elongation-at-break of cotton yarns and tire cord are influenced by prior moisture history, and whether or not preconditioning before exposure to the standard atmosphere of 65 ± 2% R.H. at 70° ± 2° F should be required. These two properties are influenced by moisture regain, which, in turn, is influenced to a large extent by the relative humidity of the test atmosphere and to a much lesser extent by whether equilibrium was approached by sorption or desorption. Preconditioning is therefore required in the test procedure for determining standard moisture regain and is generally recommended for tests of other properties influenced by it. However, for most of these properties, including breaking strength and elongation-at-break, little is known as to whether the effects of the small variations possible in moisture regain at the test humidity justify the time and effort required for preconditioning.

Preconditions

Three preconditioning procedures were selected. Two represented extremes of prior moisture history with regard to moisture regain that are likely to be encountered in routine testing. The lower humidity was approximately 29% (calculated) at 96° F, and was obtained in a drying oven in which air from the standard atmosphere was circulated without being heated. The higher humidity was 80% at 70° F, and was obtained in a desiccator containing a concentrated solution of ammonium sulfate. Moisture regains of approximately 4% and slightly higher than 10%, respectively, were produced by these two humidities, whereas under standard conditions, the moisture regains, as shown in Table I, were in general approximately 8%. The low humidity meets the requirements of the American Society for Testing Materials for determining standard moisture regain—namely, that equilibrium in the standard atmosphere shall be approached from the dry side (not moisture free) and that the lower moisture regain may be that reached at equilibrium in any atmosphere having a relative humidity between 10% and 40%.

The third procedure utilized prevailing mill conditions—approximately 60% R.H. at 78° F—and represented the usual practice at the Southern Regional Research Laboratory when testing yarns and cords directly after manufacture in the textile laboratory.

Sample Description

Duplicate sets of 1 bobbin each of 16/1, 30/1, 16/2, and 30/2 yarns and of 16/4/3 tire cord were made from Stoneville 2B cotton in the textile laboratory. The two sets were made at separate times and were tested separately. One exception was in series II, where a bobbin of tire cord that had been in the testing room for several weeks was used. Its intermediate preconditioning was therefore 65% R.H. at 70° F instead of 60% R.H. at 78° F.

Procedure

The two sets of yarns and tire cords were each subjected to each of the three preconditions for at least 24 hrs. and were then exposed for a minimum of 24 hrs. to the standard test atmosphere before they were tested for breaking strength and elongation. In addition, moisture regains were determined under the conditions of test.

In series I, 250 individual tests for strength and elongation were conducted on each yarn in units of 50 tests each, and 120 tests on the tire cord in units of 40 tests. In series II, 200 tests of

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TABLE I. BREAKING STRENGTH, ELONGATION, AND MOISTURE REGAIN OF PRECONDITIONED COTTON YARNS AND TIRE CORDS TESTED UNDER STANDARD CONDITIONS

	Breaking strength*			Elongation at break*			Moisture regain*		
	Preconditioned at R.H. of:			Preconditioned at R.H. of:			Preconditioned at R.H. of:		
Sample description	29% (g.)	60% (g.)	80% (g.)	29% (%)	60% (%)	80% (%)	29% (%)	60% (%)	80% (%)
16/1 yarn									
Series I	539	541	552	6.01	5.96	6.21	7.26	7.31	8.25**
Series II	537	530	532	5.69	5.68	5.89	7.23	7.33	8.17
Average	538	536	542	5.85	5.82	6.05	7.24	7.32	8.21
30/1 yarn									
Series I	248	241	252	4.84	4.87	5.12	7.72	7.61	8.42**
Series II	304	308	303	6.03	5.93	5.76	7.51	7.62	8.30
Average	276	275	276	5.44	5.40	5.44	7.62	7.62	8.36
16/2 yarn									
Series I	1102	1106	1103	6.61	6.40	6.65	7.19**	7.28**	8.22**
Series II	1108	1112	1115	4.62	4.62	4.82	7.16	7.24	7.98
Average	1105	1109	1109	5.62	5.51	5.74	7.18	7.26	8.10
30/2 yarn									
Series I	554	542	550	5.31	5.30	5.32	7.24**	7.38**	8.04**
Series II	593	594	596	5.14	5.64	5.14	7.20	7.31	7.96
Average	574	568	573	5.22	5.47	5.23	7.22	7.34	8.00
16/4/3 tire cord	(lbs.)	(lbs.)	(lbs.)						
Series I	24.5	24.4	24.6	6.67	6.52	6.67	8.00	8.16	—
Series II	25.4	25.4	25.2	5.44	5.61	5.63	8.11	8.11	8.05
Average	25.0	24.9	24.9	6.06	6.06	6.15	8.06	8.14	8.05

* The values for breaking strength and elongation of the different yarns are the averages of 250 tests for series I and of 200 tests for series II. Those for the tire cord are the averages of 120 tests for series I and of 200 tests for series II. The values for moisture regain in series I are the averages of 2 determinations except for those marked**, indicating insufficient material for more than 1 test. In series II, averages of 4 determinations are given. The averages reported are the averages of the two series and not of the individual determinations.

each yarn and cord were made, units of 50 tests being used. Moisture determinations for series I were made in duplicate when the supply of materials permitted, and for series II, in quadruplicate.

Breaking strength and elongation were determined in the conventional manner, using pendulum-type testers. The yarn tester had a triple capacity of 0–500, 0–1,000, and 0–2,000 g., and the tire-cord tester a double capacity of 0–25 and 0–50 lbs. Elongation of the yarns was read directly from the tester and of the tire cord from autographically recorded charts.

A forced-draft oven with a balance on top was used for determining moisture regain.

Discussion

The results of the tests are given in Table I.

The breaking strength and elongation values for both the yarns and the cords showed no definite trend that could be attributed to the preconditioning humidity. The differences within a series were relatively small and are within the magnitude of errors due to nonuniformity in the yarns and cords and the experimental errors inherent in the conditions of test rather than to any possible effects of preconditioning. The larger differences found between the two series are accounted for by the different lots of samples.

As was expected, the moisture regains were generally higher, the higher the preconditioning humidity, although the differences were not large. The largest differences were observed between the yarns that attained equilibrium in the standard atmosphere by sorption and those by desorption. The fact that almost identical values were obtained on yarns preconditioned at approximately 29% R.H., in conformance with A.S.T.M. recommendations, and on those taken directly from the prevailing mill conditions supports present practice of not preconditioning. The interpretation of the moisture-regain values for the tire cord is not definite, but the absence of trends that can be attributed to prior moisture history of the cord indicates that

preconditioning had no significant effect on the test values.

The results reported here indicate that under usual test conditions, where moisture regain is within the 4% to 10% observed in these samples, preconditioning so that moisture equilibrium in the standard atmosphere is approached from a lower regain is not necessary before determining breaking strength and elongation-at-break of cotton yarns and tire cord. This conclusion, however, should not be over-generalized by application to conditions other than those specifically described. When high-precision tensile testers are to be used, for example, or when other properties that are influenced by moisture regain are to be measured, the need for preconditioning should again be considered.

(*Manuscript received September 25, 1950.*)

Gordon Research Conferences

THE TEXTILES CONFERENCE of the Gordon Research Conferences, sponsored by the American Association for the Advancement of Science, will again be held at Colby Junior College, New London, New Hampshire, the week of July 16.

Individuals interested in attending the Conference are requested to send in their applications to W. George Parks, Director, Department of Chemistry, Rhode Island State College, Kingston, Rhode Island, on or before May 1, 1951. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance at each Conference is limited to 100. From June 15 to September 1, 1951, mail should be addressed to Colby Junior College, New London, New Hampshire.

The program for the 1951 Textiles Conference is as follows:

Joseph H. Brant, *Chairman*

Walter J. Hamburger, *Vice-Chairman*

July 16—T. Waller George	—"Localized Plastic Flowing in Filamentous Solids"
Lyman Fourt	—"Obtaining and Measuring Luster in Cotton"
July 17—Eugene Pacsu	—"A Critical Discussion of the Structural Problem of Cellulose"
W. E. Roseveare	—"The Structure and Reactivity of Cellulose"
July 18—L. P. Herrington	—"The Physiology of Clothing"
J. R. Whinfield	—"Terylene"
July 19—Milton Platt	—"Some Factors Affecting the Translation of Fiber Properties into Yarn Systems"
Ralph G. H. Siu	—"Practical Implications of Studies on the Biochemical Mechanism of Cellulose Breakdown by Microorganisms"
July 20—James Wakelin and Herbert Haller	—"Research Studies and Processing Trials on Various Wools"
July 22, 8:00 P.M.	—Public lecture—Subject and speaker to be announced

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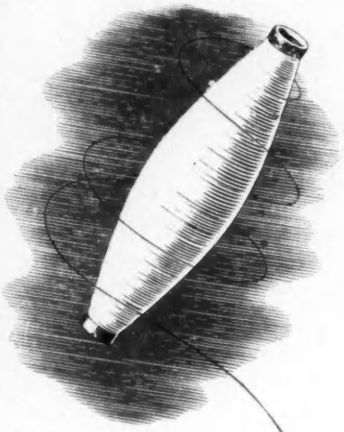

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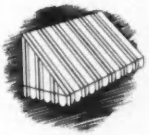

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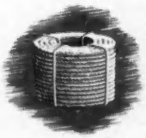

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